

METHODS FOR SULFATE AIR QUALITY MANAGEMENT

Volume 1.
Executive Summary

by

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with

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ABSTRACT

A study of methods for sulfate air quality control strategy design has been conducted. Analytical tools developed were tested within a case study of the nature and causes of the high sulfate concentrations observed in the Los Angeles area. A principal objective was to investigate the least costly means for sulfate air quality improvement in that locale.

A long-run average emissions to air quality model was derived which computes pollutant concentrations from Lagrangian marked particle statistics based on the time sequence of measured wind speed, wind direction, and inversion base motion. Physical assumptions drawn from analysis of existing air quality and meteorological data were used to adapt this model to a specific application -- sulfate air quality prediction in Los Angeles. An energy and sulfur balance on the fate of energy resources containing sulfur was developed to test the consistency of a sulfur oxides emissions inventory for that air basin. Then material balance arguments were used to trace sulfur flows within that regional energy economy through the air quality model which also conserves sulfur mass. Sulfate air quality model predictions were compared to historical observations

over the years 1972 through 1974. The sulfate air quality impact of individual emission source classes was estimated at a large number of air monitoring sites.

A hybrid theoretical-empirical model was constructed which explains the relationship between sulfate air quality and prevailing visibility at Los Angeles. An estimate was made of the visibility improvement which would have accrued if Los Angeles sulfate concentrations were reduced by 50 percent on each past day of record. Then two emissions control strategy example calculations were performed to illustrate the means by which the air quality model results could be used to evaluate the cost of attaining such an air quality improvement.

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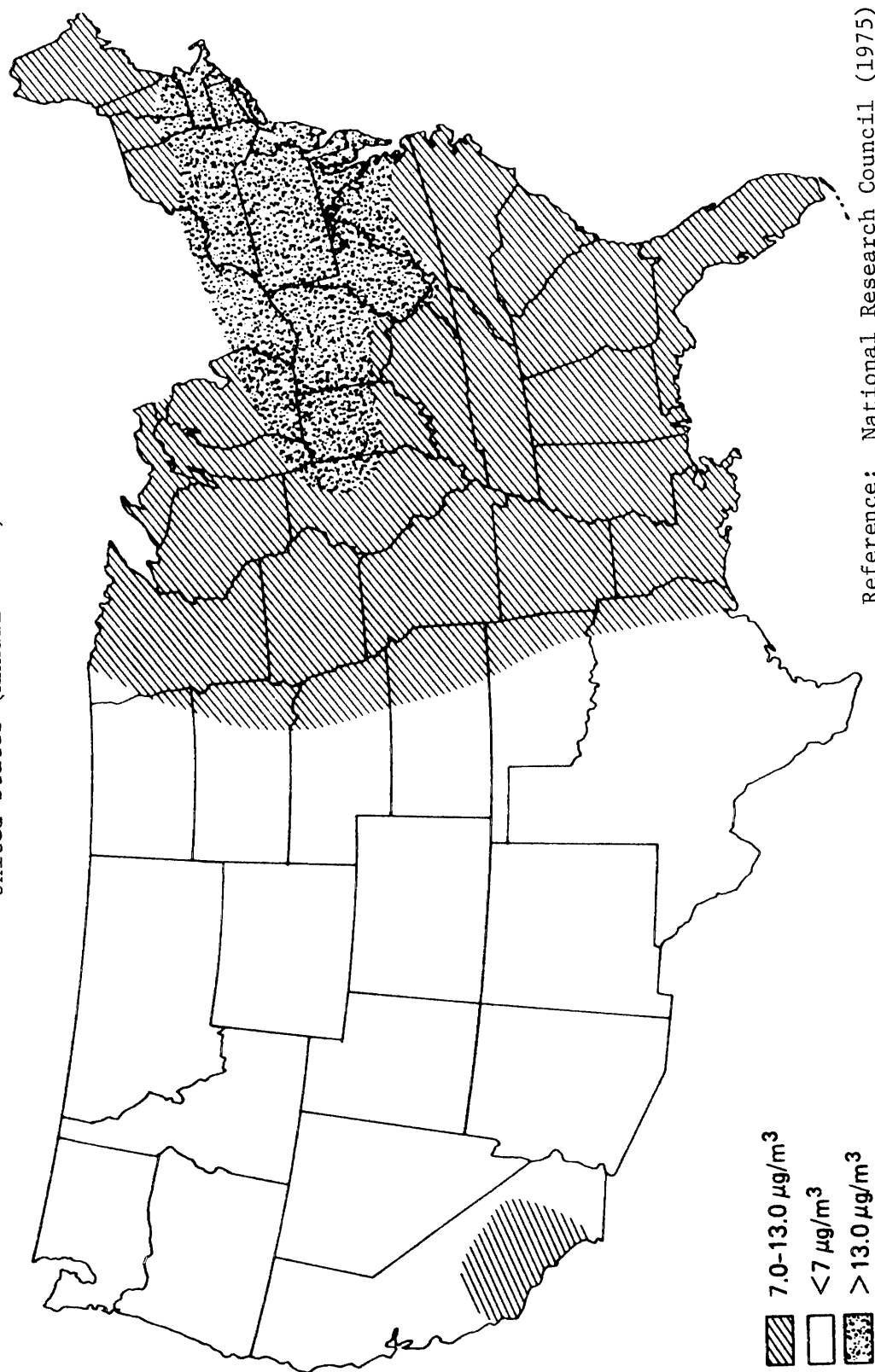
1.0 Introduction

A study of particulate sulfate air quality control opportunities in the South Coast Air Basin has been conducted. The principal objectives of that study were to obtain a physical description of the nature and causes of the high sulfate concentrations observed in the Los Angeles area, and to investigate the least costly means for sulfate air quality improvement in that locale.

Particulate sulfates accounting for a few percent of the sulfur content of fuel are emitted directly from most combustion processes. Additional sulfates form from atmospheric oxidation of SO_2 downwind from a sulfur oxides source. These water-soluble sulfur oxides particles accumulate in a size range around 0.5 microns in diameter in the Los Angeles atmosphere (Hidy et al., 1975). Particles of this size are extremely effective scatterers of light (Middleton, 1952), and also are capable of deep penetration into the lung (Task Group, 1966). Recent studies indicate that sulfates contribute to visibility deterioration (Eggleton, 1969; Charlson et al., 1974; Waggoner et al., 1976; Weiss et al., 1977; White and Roberts, 1977) and to the acidification of rain water (Cogbill and Likens, 1974; Likens, 1976) throughout the United States and in Europe.

In Figure 1, it is seen that two areas of the United States are affected by high sulfate concentrations: the entire Eastern United States and portions of southern California. The Los Angeles

Figure 1
Geographic Distribution of Typical Urban Sulfate Levels in the
United States (Annual Means)



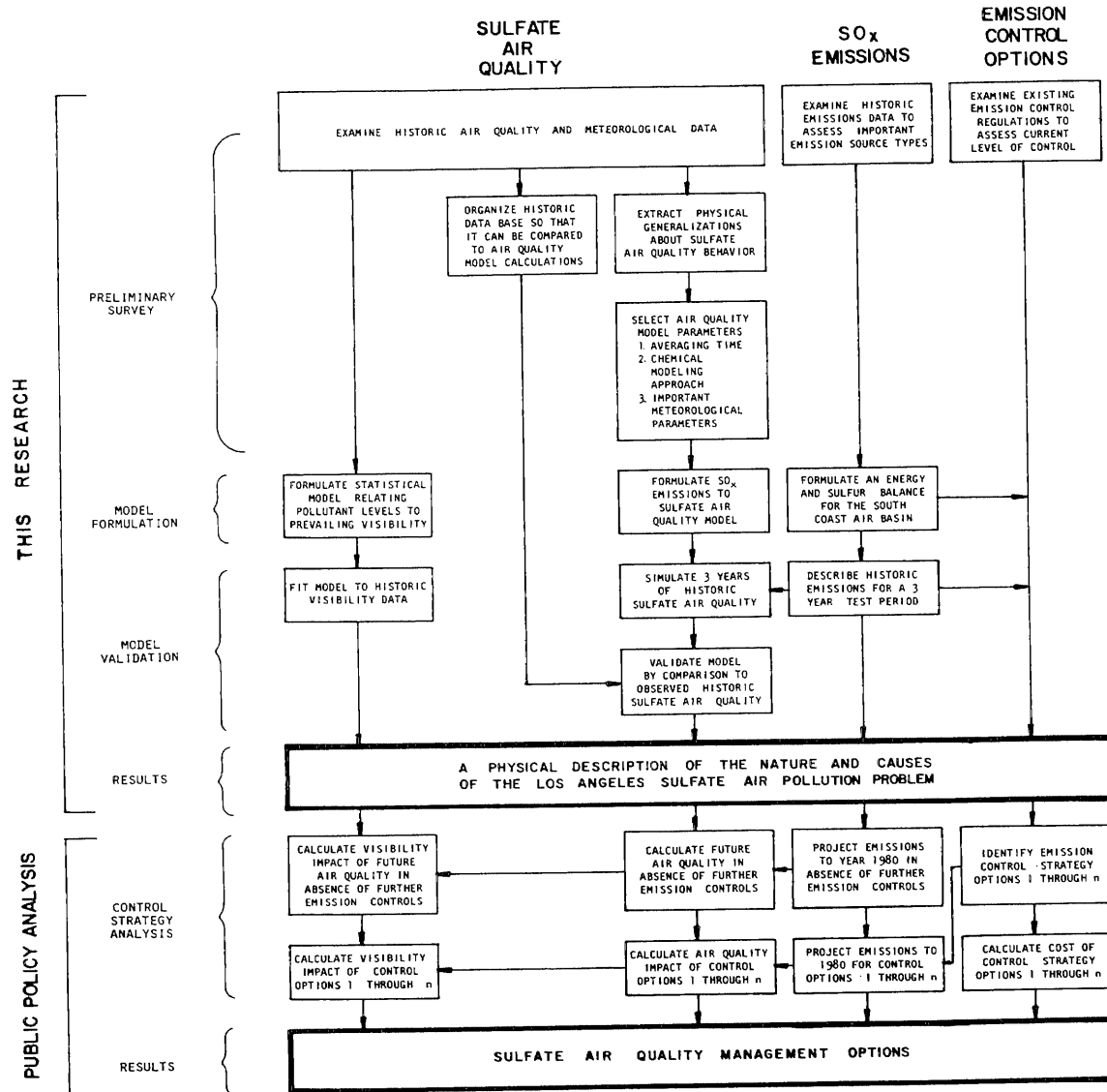
sulfate problem presents an excellent choice for a case study of sulfate air quality control opportunities because it is self-contained: it spans a small enough geographic area that one can draw a box around it and analyze it in great detail. In the process, insights will be acquired that should help those charged with control of sulfate air quality problems of great geographic extent in the Eastern United States and in Europe.

The research plan for this study is shown in the upper portion of Figure 2. Mathematical models relating sulfur oxides emissions to sulfate air quality and to effects on visibility are verified against historical monitoring data. Examples are then given to show how those models can be used to define the least costly path toward sulfate air quality improvement. Findings established in pursuit of that research plan are described in this Executive Summary.

2.0 Characteristics of Sulfate Air Quality in the South Coast Air Basin

The geographic region of interest is the South Coast Air Basin which surrounds Los Angeles. Air quality data from twenty-seven sampling sites at locations shown in Figure 3 have been analyzed as part of this study. Particular attention was paid to the years 1972 through 1974. During those years, the Los Angeles Air Pollution Control District (LAAPCD), EPA's CHES program and the National Air Surveillance Network monitoring programs operated concurrently yielding the widest geographic coverage of sulfate air quality data available at the start of this investigation.

Figure 2
Research Plan



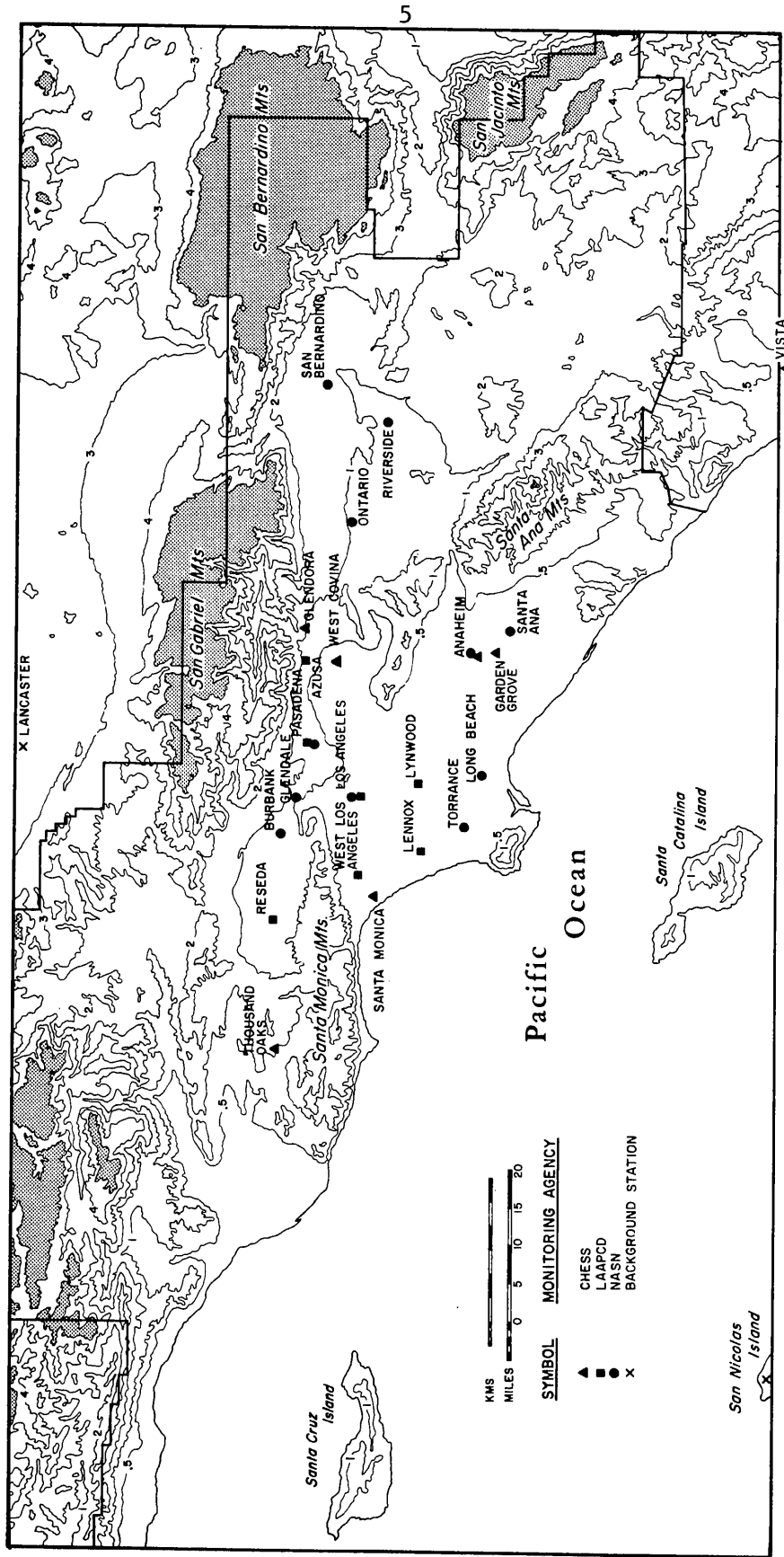


Figure 3
 Sulfate Air Quality Monitoring Sites in or near the South Coast Air Basin

Spatial gradients in sulfate air quality indicate that the atmosphere over metropolitan Los Angeles is enriched in sulfates due to local emissions sources. Annual mean sulfate concentrations above $14 \mu\text{gm}/\text{m}^3$ were measured over central Los Angeles at a time when background concentrations in incoming marine or desert air averaged 3 to $5 \mu\text{gm}/\text{m}^3$. This localized sulfate enrichment is illustrated in Figure 4. In contrast to the problems arising from long distance transport of sulfates in the Eastern United States, a sulfate air quality model can be validated in the South Coast Air Basin while employing only local emissions data plus a small increment from background sulfates.

Sulfate concentrations observed at the downtown Los Angeles station of the Los Angeles Air Pollution Control District during the decade 1965 through 1974 are shown in time series in Figure 5a. Concentration fluctuations from day to day are quite large, with high values occurring at least occasionally in all seasons of the year. However, the data can be filtered statistically to reveal seasonal trends, as shown in Figure 5b. It is seen that a broad summer seasonal peak in sulfate concentrations occurs in all years of record, with clusters of very high sulfate concentrations also observed in two of nine winters examined (winter 1970-71 and winter 1971-72). A successful air quality control strategy study must consider both high summer and high winter sulfate conditions in the Los Angeles area.

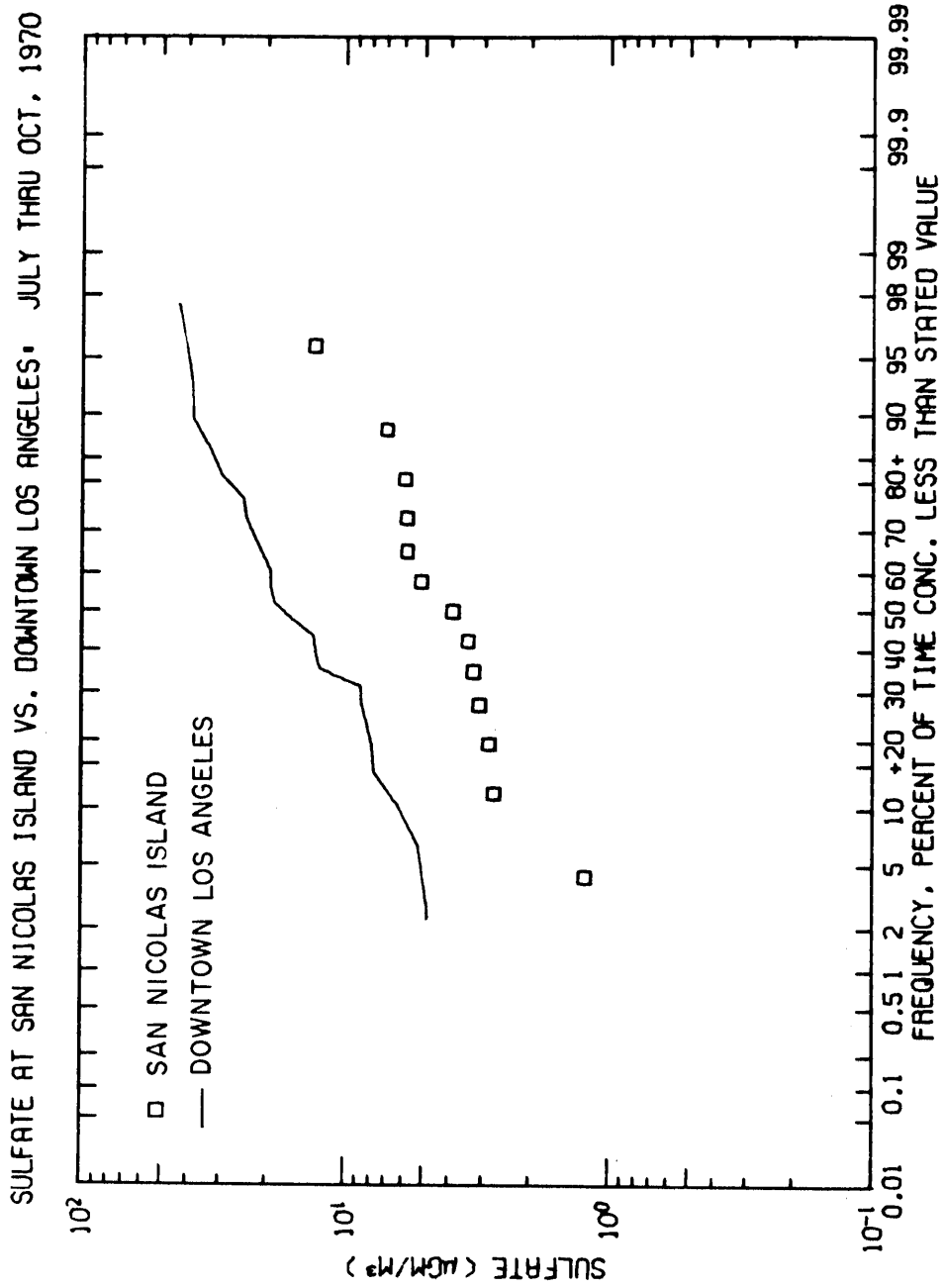


Figure 4

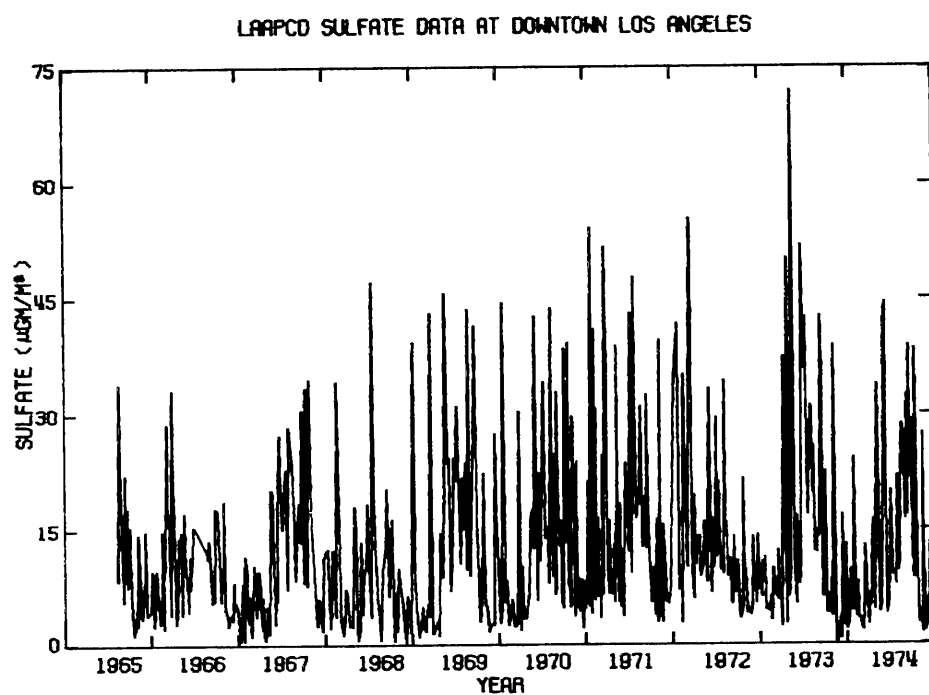


Figure 5a

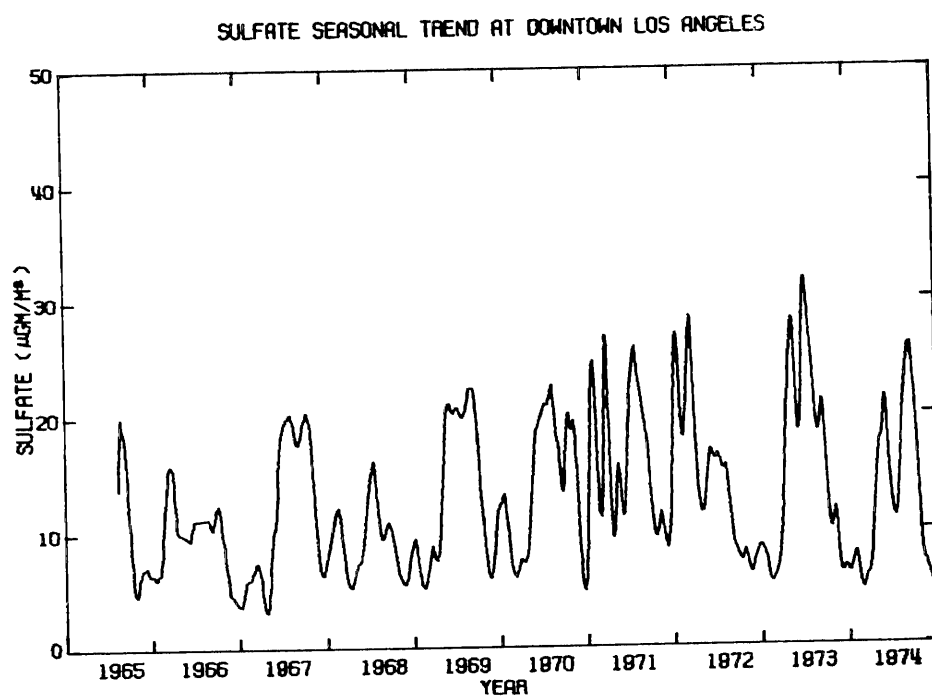


Figure 5b

In Figure 6, the same filtering process has been applied to the LAAPCD and CHES data at all monitoring stations active during the period 1972 through 1974. The similarity of seasonal pollutant patterns is quite striking. Simultaneous 24-hour average sulfate concentrations at widely separated monitoring stations are of nearly equal magnitude and are highly correlated, as shown by the graphs in Figure 7. Temporal trends in the available sulfate air quality data base are more pronounced than average spatial gradients. When constructing a model which must explain the dynamic nature of Los Angeles sulfate air quality, concentration predictions made in time series should be emphasized.

The ability of available field data to verify time series air quality predictions was investigated statistically. From analysis of measurement errors and sampling frequency it was found that sulfate air quality predictions made over monthly and longer averaging times could be verified closely. Therefore, an air quality model for monthly average sulfate concentrations will be sought.

A mass balance on the fate of sulfur oxides emissions in Los Angeles constructed by Roberts (1975) and summarized in Table 1 shows that emissions of both primary sulfates and SO_2 must be considered. Ground level deposition of sulfur oxides is a significant removal mechanism. The atmospheric oxidation of SO_2 to form additional sulfates must be included within our air quality model in order to account for total observed sulfate concentrations.

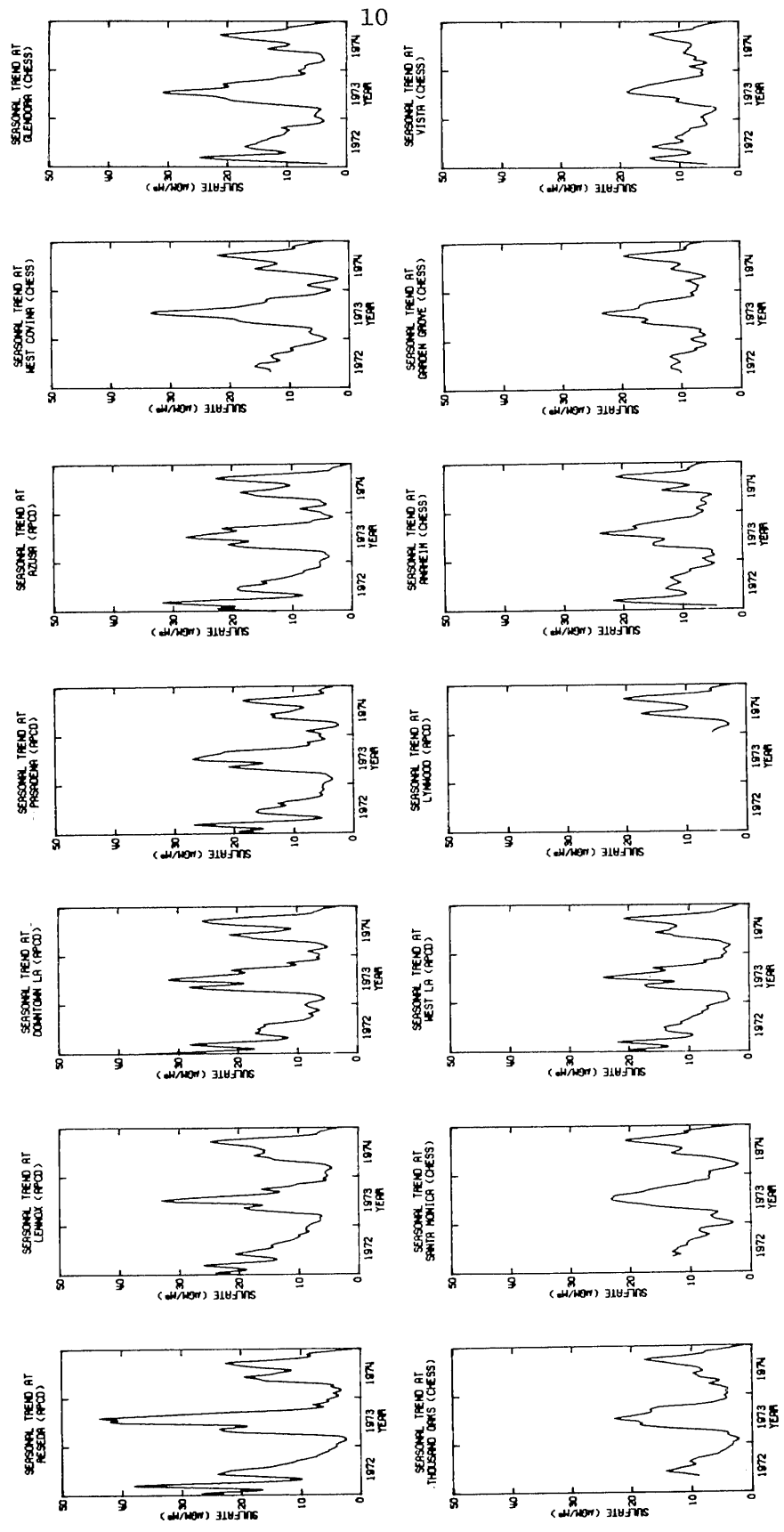


Figure 6
Seasonal Trends in Sulfate Air Quality 1972 through 1974

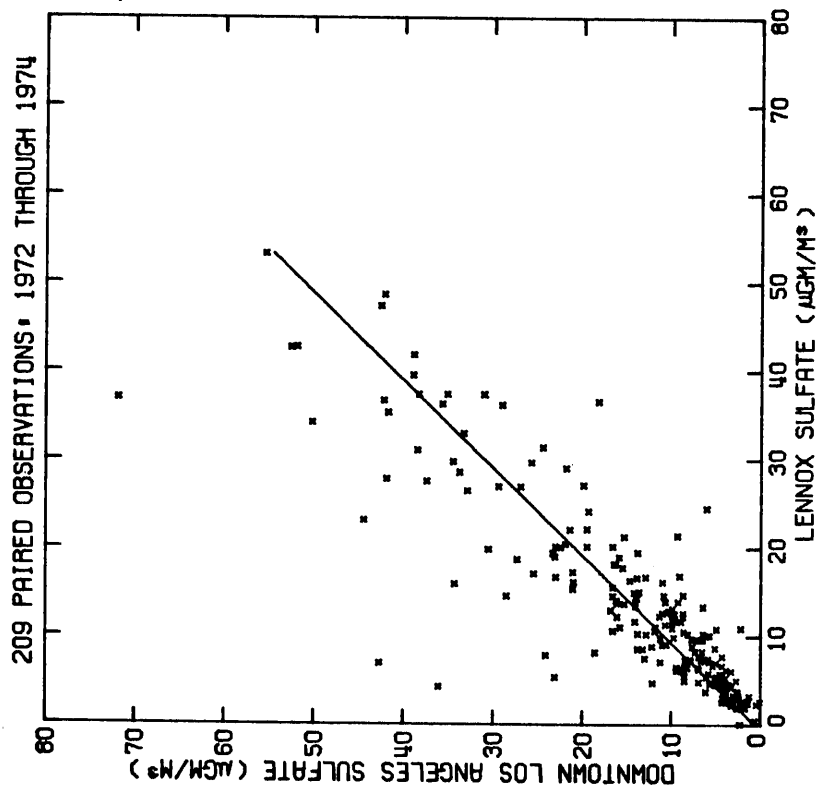


Figure 7a

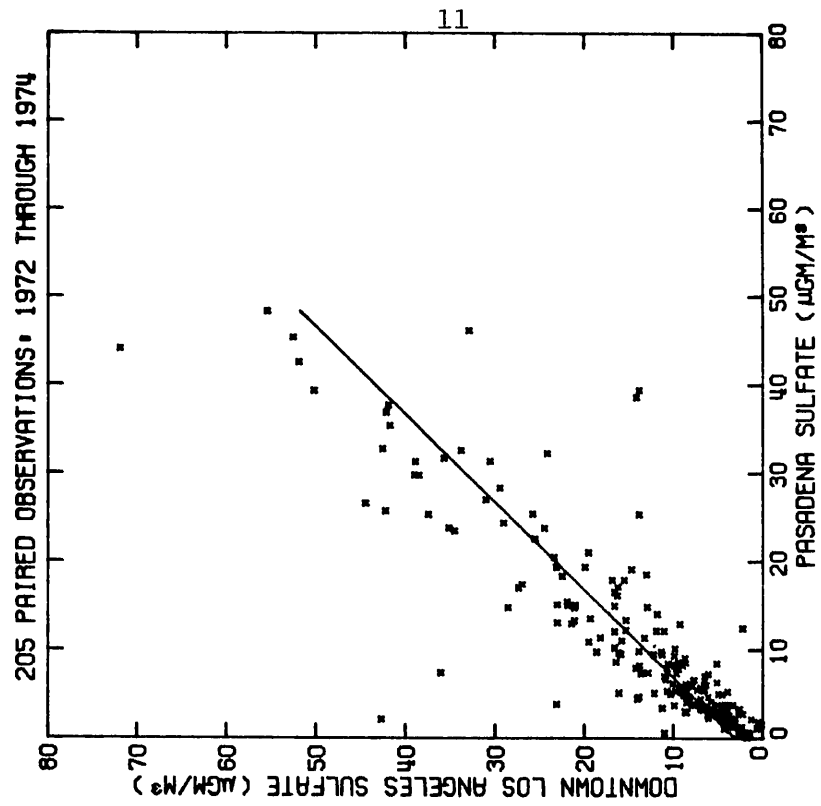


Figure 7b

TABLE 1

Material Balance⁽¹⁾ on the Fate of
Sulfur Oxides in Los Angeles on July 25, 1973
(from Roberts, 1975)

	Sulfur Oxides (in metric tons per day stated as SO ₂ equivalents)
Sources	
SO ₂ Emissions	419
Primary Sulfate Emissions	less than 22
Background Sulfates	<u>7</u>
	less than 448
Fate	
Ground Level Dry Deposition of SO ₂	248
Ground Level Dry Deposition of SO ₄ ⁼	5
SO ₂ Remaining Airborne	115
SO ₄ ⁼ Airborne	<u>57</u>
	425

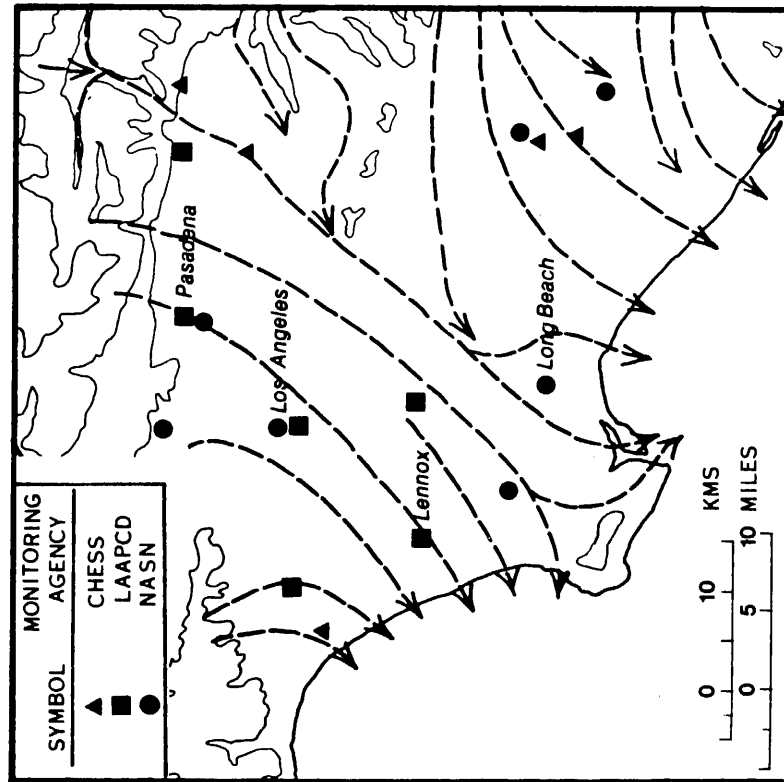
(1) Source and fate estimates obtained independently, hence perfect agreement not expected

In order to select a chemical modeling approach, atmospheric sulfur oxides air chemistry first was reviewed. Then sulfate concentration changes from day-to-day were compared to fluctuations in the other observable components of the likely chemical oxidation processes. Sulfate concentration changes were shown to closely track changes in relative humidity and total suspended particulate levels, with intrusion of fog on days of very high sulfate concentration. This suggests that heterogeneous oxidation of SO_2 on or within wetted particles is important to days of high sulfate concentration in Los Angeles. Sulfate concentrations also were found to be significantly higher on days of elevated oxidant concentrations. Thus gas phase oxidation of SO_2 by free radicals present in Los Angeles photochemical smog probably also is important.

While procedures exist which would permit computation of gas phase SO_2 oxidation rates from first principles, data on catalyst concentration and ammonia levels needed to calculate heterogeneous phase SO_2 oxidation rates on or within wetted particles are lacking. Fortunately, the pseudo-first order rate of SO_2 oxidation in the Los Angeles atmosphere due to all chemical processes combined was measured during field experiments conducted in 1973. Thus it was decided that chemical conversion of SO_2 to form sulfates should be modeled as a slow pseudo-first order reaction within the range of existing experimental data on the rate of sulfate formation in the Los Angeles atmosphere.

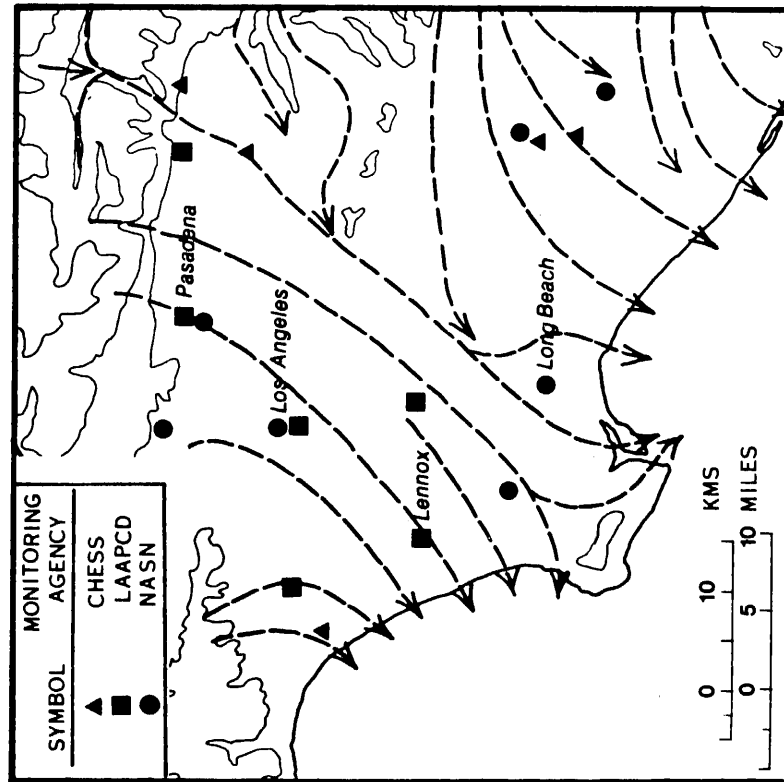
Ambient monitoring data also were studied to identify the meteorological processes which most directly affect sulfate transport and dispersion. The Los Angeles Basin is influenced by coastal meteorology characterized by a daily sea breeze/land breeze wind reversal. Differential heating of land and sea surfaces leads to a daytime wind pattern with transport inland across the coastline as shown in Figure 8a. At night the characteristic transport pattern reverses as seen in Figure 8b. Slow drainage winds and land breeze conditions cause flow out to sea. As a result, vector average wind speed (which determines air parcel retention time in the basin) is typically less than half of the apparent scalar wind speed observed, as shown in Table 2. From analysis of air parcel trajectories, it was found that a trajectory integration time of two days would be needed to insure that 95 percent of the air parcels of that age are advected to beyond the boundaries of the 50 by 50 mile square area pictured in Figure 8. Even slow atmospheric chemical reactions would proceed toward completion over such long retention times in the air basin.

Afternoon inversion base height was shown to govern the extent of vertical dilution for sulfates within this airshed. In the mornings, inversion base height is often low enough that emissions from elevated sources are injected above the mixed layer of the air basin for many hours. Thus it was found that the key meteorological factors which must be incorporated into the transport portion of our air



(a)
Typical Afternoon Onshore Flow Pattern
July 12:00-18:00 Hours PST

Figure 8a



(b)
Typical Late Night Offshore Flow Pattern
October 00:00-07:00 Hours PST

Figure 8b

(after DeMarrais, Holzworth and Hosler, 1965)

Table 2

Monthly Resultant Wind Data
For Long Beach During the
Years 1972 through 1974

Month	Resultant Wind Speed Computed after Progressive Vector Addition of Successive Wind Observations for Each Month (miles per hour)			Scalar Average of Wind Velocity Observations (miles per hour)		
	1972	1973	1974	1972	1973	1974
January	0.4	1.0	1.0	5.6	6.4	4.8
February	0.9	1.4	1.2	5.2	6.5	5.4
March	2.5	4.3	2.5	6.0	8.2	5.2
April	2.7	2.8	3.5	6.2	8.1	5.7
May	3.4	3.2	3.1	6.9	6.4	5.7
June	3.8	3.1	2.7	7.3	6.4	5.3
July	3.0	2.9	2.7	7.1	5.8	5.4
August	2.8	2.8	2.6	6.7	6.1	5.4
September	3.2	2.6	1.6	6.8	6.2	3.3
October	2.0	2.1	2.6	5.7	5.6	5.4
November	1.3	1.5	1.9	5.5	5.1	4.9
December	2.1	0.6	0.6	6.2	3.0	5.3

Source: U.S. Department of Commerce (1972 through 1974)

To convert miles per hour to meters per second, multiply by 0.45.

quality model include inversion base motion as well as vector valued wind.

3.0 Air Quality Model Development

Most existing long-term average air quality models lack the ability to reproduce those conditions most important to sulfate air quality in a coastal region like Los Angeles. Pseudo-steady state models which employ a joint frequency distribution of wind speed, wind direction and atmospheric stability have no hope of correctly computing air parcel retention time in an air basin characterized by a daily sea breeze/land breeze reversal in wind direction. That is because those models contain no information about the serial correlation of the wind vectors.

Therefore a new type of simulation model was derived for directly calculating long-run average sulfate air quality under unsteady meteorological conditions. The model computes pollutant concentrations from long-run average source to receptor transport and reaction probabilities. These transport and reaction probabilities in turn were estimated from Lagrangian marked particle statistics based on the time sequence of historical measured wind speed, wind direction, and inversion base height motion within the airshed of interest. First order chemical reactions and pollutant dry deposition were incorporated. The model was adapted to a multiple source urban setting in a way which permits retention of the air quality impact of each source class contributing to air quality predictions at each receptor site.

The calculation procedure used in that air quality model can be summarized briefly. Single particles marked with the magnitude and initial chemical composition of sulfur oxides emissions from each source are inserted at measured time intervals into the atmosphere above the location of their points of origin. Depending on the plume rise characteristics of each source and meteorological conditions at the time of release, a pollutant parcel may be inserted either above or below the base of the temperature inversion which separates a well mixed layer next to the ground from a stable air mass aloft.

As these sulfur oxides laden air parcels are transported downwind, chemical reactions and surface removal processes act to alter the mass of SO_2 and sulfates represented by each particle. Sulfur oxides residing within the mixed layer next to the ground are affected both by ground level dry deposition and by atmospheric oxidation of SO_2 to form additional sulfates. Pollutant parcels stored within the stable layer aloft are isolated from surface removal processes but still are available for chemical reaction. Exchange of air parcels between the mixed layer next to the ground and the stable layer aloft occurs as inversion basing height changes over time, as pictured in Figure 9.

Transport calculations in the horizontal plane are described schematically in Figure 10. The trajectories of successive particles released from a source form streaklines downwind from that source. Streaklines present at each hour of the month are computed and superimposed. The horizontal displacement of each particle located

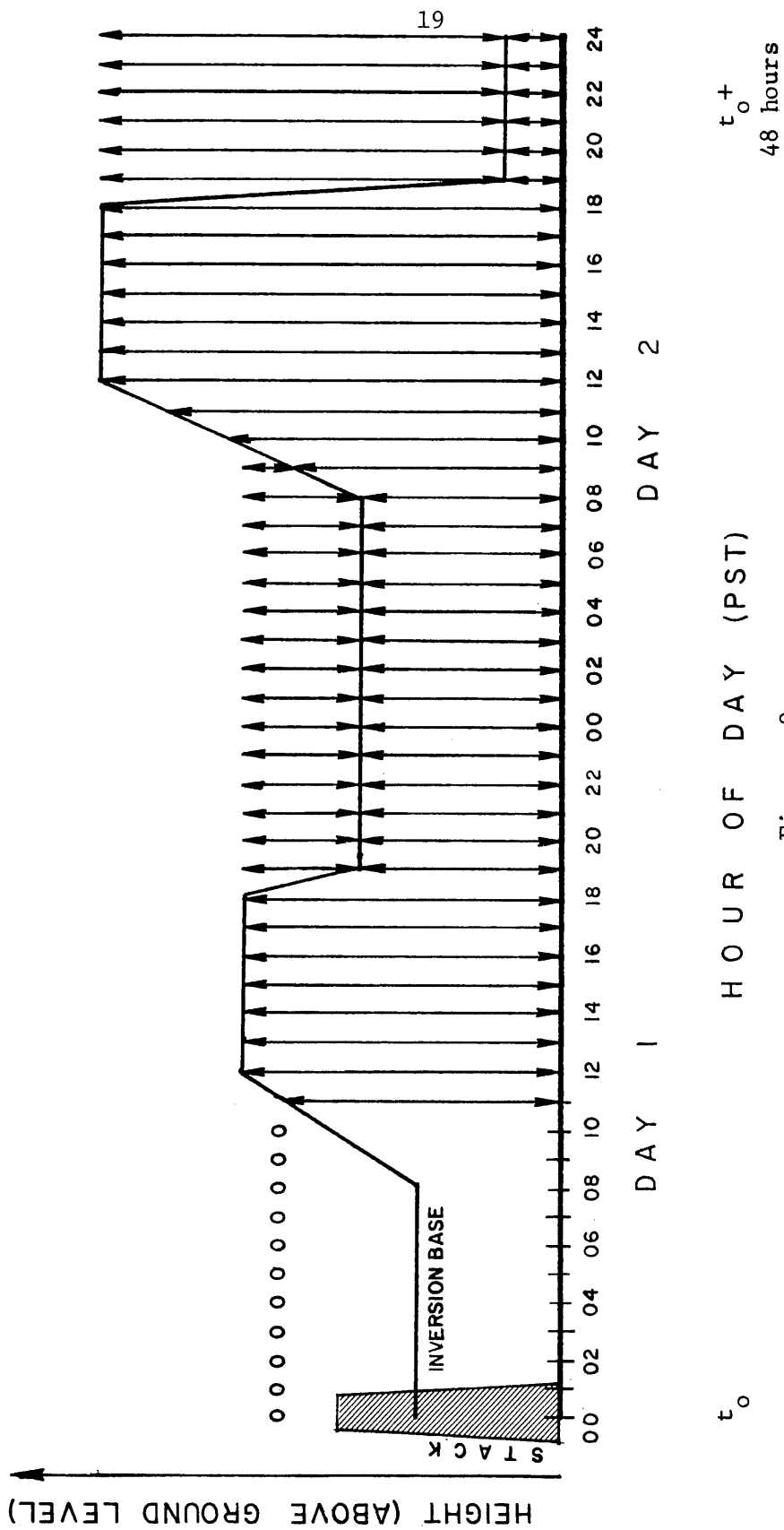
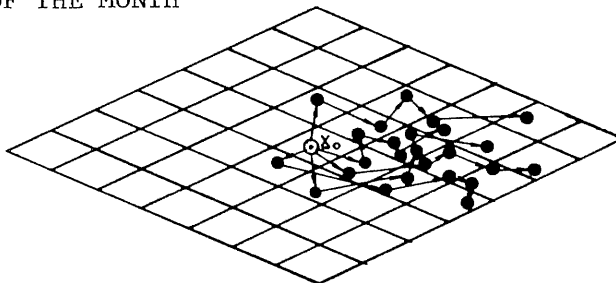


Figure 9

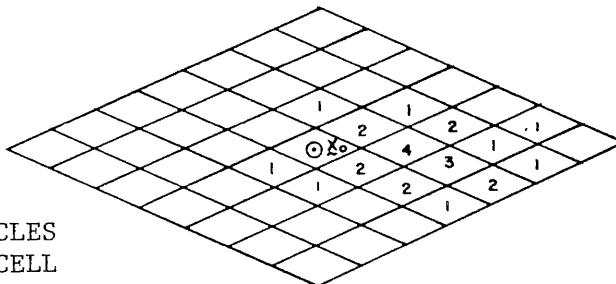
Hypothetical Time History of Interaction Between the Inversion Base and a Fluid Particle Released at Time t_o (o's indicate a single particle stabilized within the inversion; zone between arrows (\uparrow) indicates that vertical mixing has occurred while the particle resided below the inversion base).

STEP 1

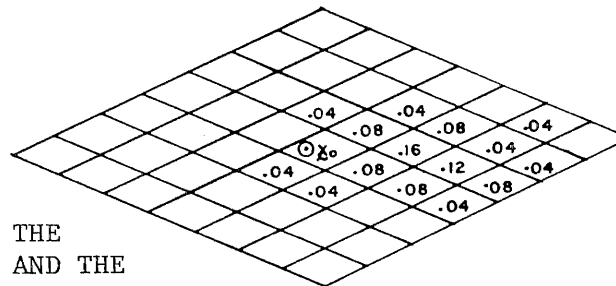
LOCATE PARTICLES WITHIN THE CELLS OF A RECEPTOR GRID



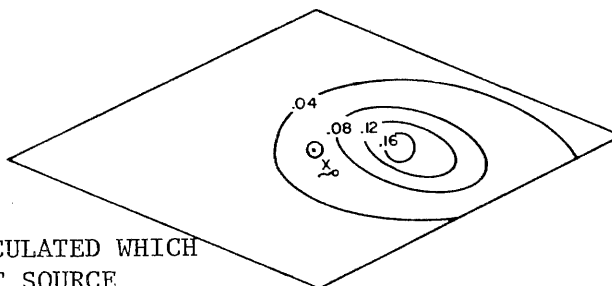
ACCUMULATE THE MAGNITUDES
ASSOCIATED WITH THE PARTICLES
FALLING WITHIN EACH GRID CELL



DIVIDE THE ACCUMULATED
POLLUTANT MASS LOADING BY THE
SIZE OF THE RECEPTOR CELL AND THE
NUMBER OF "HOURS" BEING SUPERIMPOSED



THE SOURCE TO RECEPTOR
RELATIONSHIP HAS BEEN CALCULATED WHICH
MAPS EMISSIONS FROM A UNIT SOURCE
AT LOCATION X_0 INTO AVERAGE POLLUTANT
CONCENTRATION OBSERVED



below the inversion base is paired with the particle's probable chemical status and divided by the depth of the mixed layer at the time that the streakline of interest was computed. The resulting magnitudes are assigned to a matrix of receptor cells by summing the contribution for all particles falling within the same receptor cell. Totals are accumulated separately for SO_2 and for sulfates. The accumulated totals are divided by the dimensions of a receptor cell and the number of time steps being superimposed in order to directly obtain the spatial distribution of long-term average SO_2 and sulfate concentrations appearing throughout the airshed.

By repeating that process for each source in the airshed and superimposing the results onto an estimate of sulfate background air quality, a multiple source urban air quality model for sulfates is obtained. Superposition is permitted because all chemical processes are modeled in a form that is linear in emissions.

Potential sources of error in this model as well as the most advanced trajectory models in use today include neglect of wind shear and neglect of the vertical component of the wind. These problems can be overcome mathematically in our model at an increase in computing cost. However, lack of appropriate measurements on winds aloft prevents incorporation of these improvements at present.

The long-run average Lagrangian marked particle air quality model has several particular merits. The model need not compute concentration averages from a real time sequence of events. The order of integration over air parcel release and transport may be arranged

to minimize computing time and intermediate data storage requirements. The calculations are very simple and completely stable over time. There are no artificial diffusion problems associated with the transport scheme employed. Pollutant mass is completely conserved. The model builds its own initial conditions by integrating backward to connect all locally-emitted air parcels in the airshed at a given time to their source. Air parcels advected beyond the edges of the receptor grid are not lost to the system. Their position is remembered but their magnitude is not accumulated to a receptor cell unless the air parcel is advected back into the region of interest. Receptor cells may be specified only over those areas where concentration estimates are desired.

When adapting the air quality model for use in Los Angeles, three approximations were made as a practical consideration aimed at conserving available computing resources. First, inversion base height above ground level over the central Los Angeles Basin was treated as being spatially homogeneous at any given time. Secondly, it was assumed that inversion base motion could be represented by a stylized diurnal cycle which passes through the known daily maximum and minimum inversion base height. Finally, at any single time, the wind field over the Los Angeles coastal plain (see the area shown in Figure 8) was approximated as a uniform parallel flow. The first and third approximations above result in a huge savings in computing time by permitting the separation of trajectory and chemical calculations

from detailed dependence on a given starting location in the airshed. Model validation results presented shortly indicate that these approximations typically do not lead to errors in sulfate concentration predictions which would exceed the error bounds on the field air quality observations against which the model was tested.

4.0 An Energy and Sulfur Balance on the South Coast Air Basin

Techniques were developed and tested for performing both energy and sulfur balance calculations on flows of energy resources containing sulfur throughout the economy of the South Coast Air Basin. This approach serves several valuable functions. First, it provides a nearly independent check on the spatially resolved emissions inventory required for air quality model validation. Next it establishes the true current emissions control strategy in the airshed by showing those points in the system where sulfur is captured or segregated into products which will not lead to pollutant emissions. That is important because emissions control may be occurring in ways not obvious from reading local emissions control regulations. Pollutant emissions are connected to energy flows in a way that control strategy questions involving fuel or process substitution can be addressed. By forcing the emissions inventory to be energy consistent, prospects for making plausible emissions forecasts are improved.

Energy and sulfur balance calculations for the South Coast Air Basin in 1973 are summarized in Tables 3 and 4. The energy balance closes almost exactly, indicating that the sources and sinks for energy resources consumed in the air basin in that year are well understood.

Table 3
South Coast Air Basin Energy Balance -- 1973
(10¹² BTU's per year)

	Electricity	Natural Gas	Crude and Unrefined Oil	NGL	LPG	Still Gas for Fuel	Gasoline	Jet Fuel	Light and Middle Distillate Fuel Oil	Residual and Middle Distillate Fuel Oil	Petroleum Coke	Lubricants	Asphalt and Road Oil	Other Hydrocarbons	Coal	Digester Gas	TOTAL
SOURCES																	
Resource base: imports plus local crude oil and natural gas production	97.3	1050.3	2182.3	20.9	14.4		69.6	4.4	81.6	127.6	5.5	12.3	0.1	4.6	57.4	2.6	3715.9
Adjustments: change in gas storage; out-of-basin electric use	-13.1	-25.2															-38.3
Subtotal	84.2	1025.1	2182.3	20.9	14.4		69.6	4.4	81.6	127.6	5.5	12.3	0.1	4.6	57.4	2.6	3694.6
TRANSFORMATION SECTOR																	
Refinery feedstock (-)			-2124.8 ^(a)	-23.9	-8.7	-149.8								-16.9 ^(b)			-2174.3
Refinery fuels (-)	-9.8	-48.5			36.1	108.4				-11.8							-219.9
Refinery production (+)							843.0	224.3	126.9	581.2	112.0	18.5	88.0	60.3			2218.7
Utility fuels (-)		-160.9							-2.7	-386.3						-0.3	-550.2
Utility production (+)	179.9																179.9
Subtotal	170.1	-209.4	-2124.8	-23.9	-8.7	-149.8	843.0	224.3	124.2	189.1	112.0	18.5	88.0	60.3	-0.3		-545.8
CONSUMED IN BASIN AS ENERGY RESOURCE																	
System uses: losses	-28.8	-20.5															-49.3
Residential/commercial	-133.8	-431.4			-6.6				-8.1	-8.1					-0.2		-588.2
Industrial (other than refinery)	-71.2	-153.9			-1.0				-15.6	-19.5					-57.2	-2.3 ^(a)	-320.7
Transportation (civilian)					-1.9		-650.3	-17.3	-59.9	-9.1							-738.5
Military							-2.2	-6.1	-6.5	-0.1							-14.9
Miscellaneous	-21.9	-8.7			-3.0				-16.5	-0.6							-48.7
Subtotal	-255.7	-614.5	-2124.8	-23.9	-12.5	-149.8	-632.5	-23.4	-106.6	-37.4					-57.4	-2.3	-1760.3
CONSUMED AS A RAW MATERIAL (c)																	
		-18.6			-8.4												-152.3
EXPORTS																	
As a commodity (by ship)			-57.5		-0.2		-47.9	-17.4	-89.7	-135.1	-109.4	-20.0	-16.5	-5.1			-518.8
As a commodity (overland)		-186.8 ^(d)					-194.7	-21.8	-52.9	-27.9							-484.1
In transport mode fuel tanks							-3.8	-111.5	-2.7	-86.0							-204.0
Subtotal		-186.8	-57.5		-0.2		-246.4	-130.7	-145.3	-269.0	-109.4	-20.0	-16.5	-5.1			-1206.9
SUMMARY																	
Total sources (+ flows)	277.2	1050.3	2182.3	20.9		158.3	932.6	228.7	210.5	708.8	117.5	30.8	88.1	64.9	57.4	2.6	
Total sinks (- flows)	-278.6	-1054.5	-2182.3	-23.9		-125.6	-898.9	-174.1	-252.6	-704.5	-109.4	-30.8	-88.1	-64.9	-57.4	-2.6	
Absolute difference	-1.4	-4.2		-3.0		-20.7	33.7	54.6	-42.1	4.3	8.1						29.3
Difference as % of sources	-0.51%	-0.40%		-14.35%		-13.03%	3.61%	23.87%	-20.0%	0.61%	6.89%						
Difference as % of total energy resources	-0.04%	-0.11%		-0.08%		-0.56%	0.91%	1.48%	-1.14%	0.12%	0.22%						0.79%

Notes: (a) Obtained by difference
(b) May include some natural gas
(c) Or put to other non-energy resource use
(d) Includes exchange with out-of-basin utility

A material balance on the sulfur supplied within those energy resources shows that:

- Virtually all of the sulfur entering the air basin in that year arrived in a barrel of crude oil.
- Nearly 50 percent of the sulfur arriving was recovered at the refinery level as elemental sulfur or sulfuric acid.
- Approximately 25 percent of the sulfur was segregated into products like petroleum coke, asphalt and exported high sulfur fuel oil which would not be burned locally.
- 4.4 percent of the sulfur supply found its way into solid or liquid wastes.
- At least 14 percent of the sulfur was emitted to the atmosphere.
- The fate of 9.4 percent of the sulfur supply was undetermined. Over 70 percent of that sulfur imbalance was due to small percentage differences between two independent estimates of total sulfur supplied in crude oil versus total sulfur reported processed by refiners. This discrepancy would not lead to a significant change in atmospheric SO_x emissions estimates.

It was demonstrated that the Los Angeles Basin in 1973 was already achieving greater than 80 percent overall control of its potential SO_x emissions. Any future emission control measures adopted must be consistent with maintaining control over all of the sulfur which could get into the air rather than just that portion which currently does become airborne.

The spatially resolved inventory of sulfur oxides emissions required for air quality model application next was compiled from a source by source accounting of pollutant emissions. A grid system was laid down over the central portion of the South Coast Air Basin as shown in Figure 11. Emissions estimates for both sulfur dioxide and primary sulfates resolved over that grid system were obtained for the twenty-six classes of mobile and stationary sources listed in Table 5 for each month of the years 1972 through 1974. Major off-grid sources at locations shown in Figure 11 also were surveyed for inclusion in the air quality model calculations. The spatial distribution of average daily total sulfur oxides emissions during 1973 illustrated in Figure 12 was obtained by overlaying similar maps developed for each source class of interest.

Figure 13 shows the time history of sulfur oxides emissions from sources located within the 50 by 50 mile square grid. An underlying increment to sulfur oxides emissions from mobile sources is observed which shows little seasonal variation. Added to that is a nearly constant contribution from miscellaneous stationary sources (principally from petroleum coke calcining kilns). Petroleum refinery process emissions are shown, mostly from refinery fluid catalytic cracking units. Emissions from chemical plants (which constituted the largest single emissions source class during 1972) decline sharply during our three year period of interest as local sulfur recovery and sulfuric acid plants added new emissions control equipment.

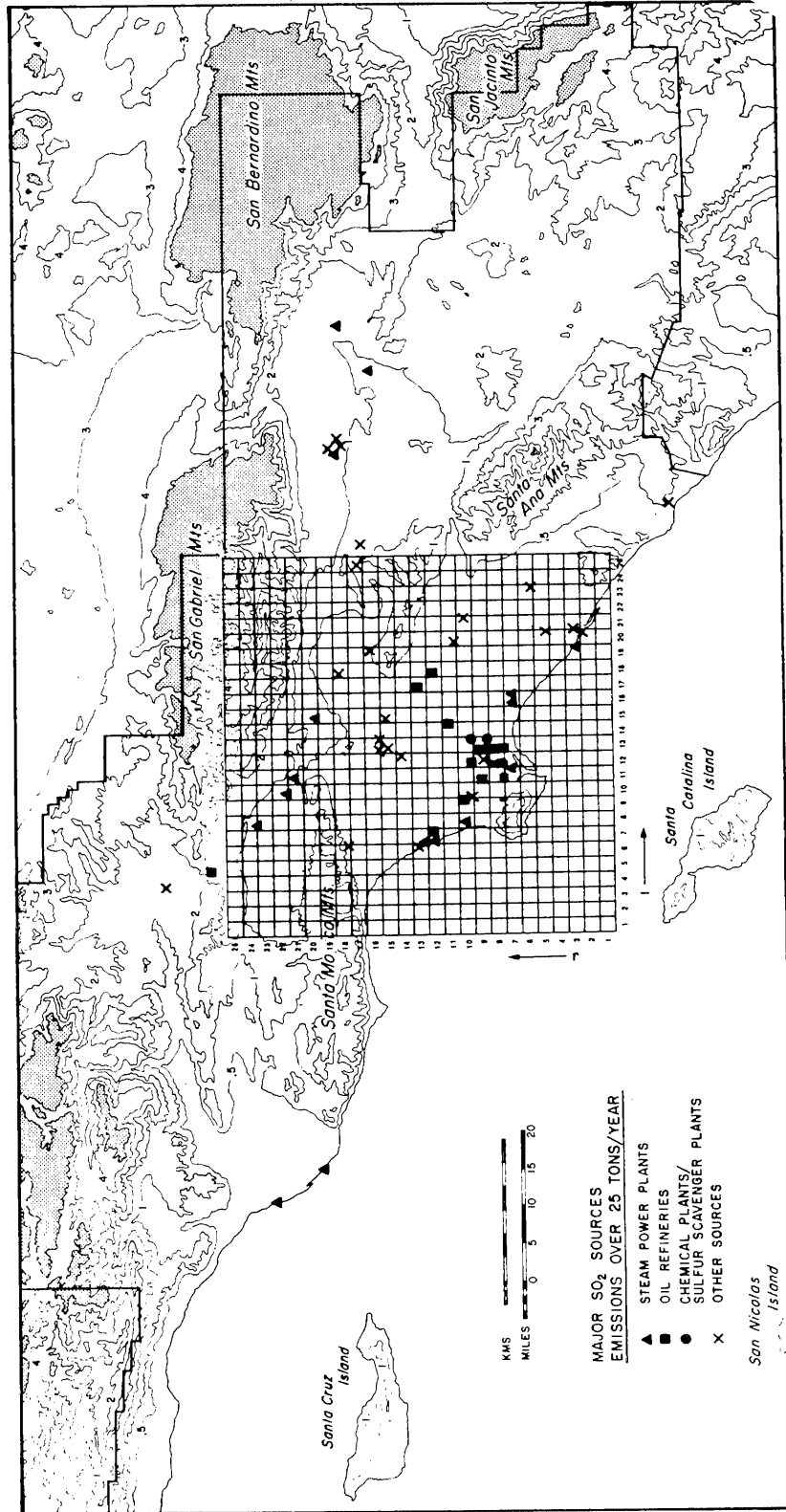


Figure 11

The Central Portion of the South Coast Air Basin
Showing the Grid System Used

TABLE 5a

1973 Sulfur Oxides Emissions Within the 50 by 50 Mile Square Grid (in short tons per day as SO ₂)													
STATIONARY SOURCES	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
Fuel Combustion													
Electric Utilities	232.77	212.31	212.13	123.36	139.48	163.87	157.77	189.23	174.16	192.05	229.72	155.48	181.71
Refinery Fuel	25.07	13.50	10.61	4.26	3.99	3.73	2.91	2.14	2.37	4.01	21.69	18.96	9.42
Other Interruptible Gas Customers	12.78	2.24	2.07	0.98	0.81	0.39	0.39	0.40	0.43	0.76	3.58	2.57	2.29
Firm Gas Customers	0.46	0.46	0.37	0.33	0.26	0.21	0.17	0.16	0.19	0.20	0.26	0.36	0.29
Chemical Plants													
Sulfur Recovery	57.18	57.18	57.18	57.18	57.08	57.08	50.70	66.20	66.20	66.20	66.20	66.20	60.40
Sulfuric Acid	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Other Chemicals	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Petroleum Refining and Production													
Fluid Catalytic Crackers	52.07	52.07	52.07	52.07	52.07	52.07	52.07	52.07	52.07	52.07	52.07	52.07	52.07
Sour Water Strippers	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
Delayed Cokers	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28
Misc. Refinery Process	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
Oil Field Production	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50
Misc. Stationary Sources													
Petroleum Coke Kilns	25.52	25.52	25.52	25.52	25.52	25.52	25.52	25.52	25.52	25.52	25.52	25.52	25.52
Glass Furnaces	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Metals Industries	8.78	8.78	8.78	8.78	8.78	8.78	8.78	8.78	8.78	8.78	8.78	8.78	8.78
Mineral Products	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sewage Treatment Digesters	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64
Other Industrial Processes	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Permitted Incinerators	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
MOBILE SOURCES													
Autos and Lt. Trucks-Surface	17.17	17.75	18.56	18.76	14.27	14.15	14.05	14.36	13.51	13.51	16.95	15.70	15.71
Autos and Lt. Trucks-Freeway	10.98	11.35	11.87	12.01	9.13	9.05	8.99	9.19	8.64	8.64	10.85	10.05	10.05
Heavy Duty Vehicles-Surface	10.18	10.50	10.94	11.05	10.99	10.88	10.99	10.99	10.35	10.34	10.71	9.90	10.64
Heavy Duty Vehicles-Freeway	6.51	6.72	7.00	7.07	7.03	6.96	6.91	7.03	6.62	6.61	6.85	6.33	6.80
Airport Operations	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06
Shipping Operations	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13	10.13
Railroad Operations	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32
TOTAL	504.73	463.64	462.36	366.63	374.67	397.95	384.27	431.33	414.10	433.95	498.44	417.18	428.94

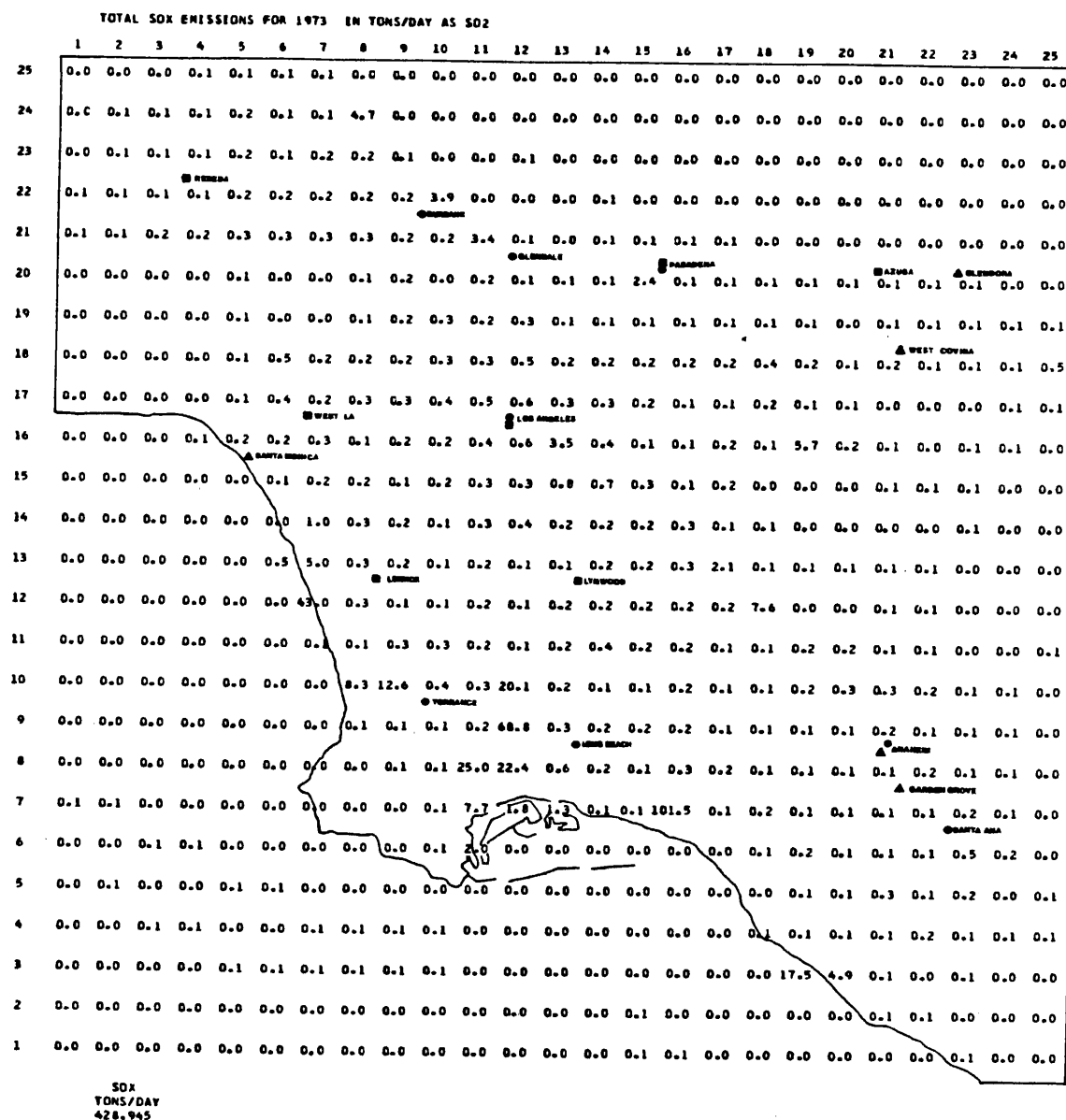


Figure 12

SULFUR OXIDES EMISSIONS WITHIN THE 50 BY 50 MILE SQUARE

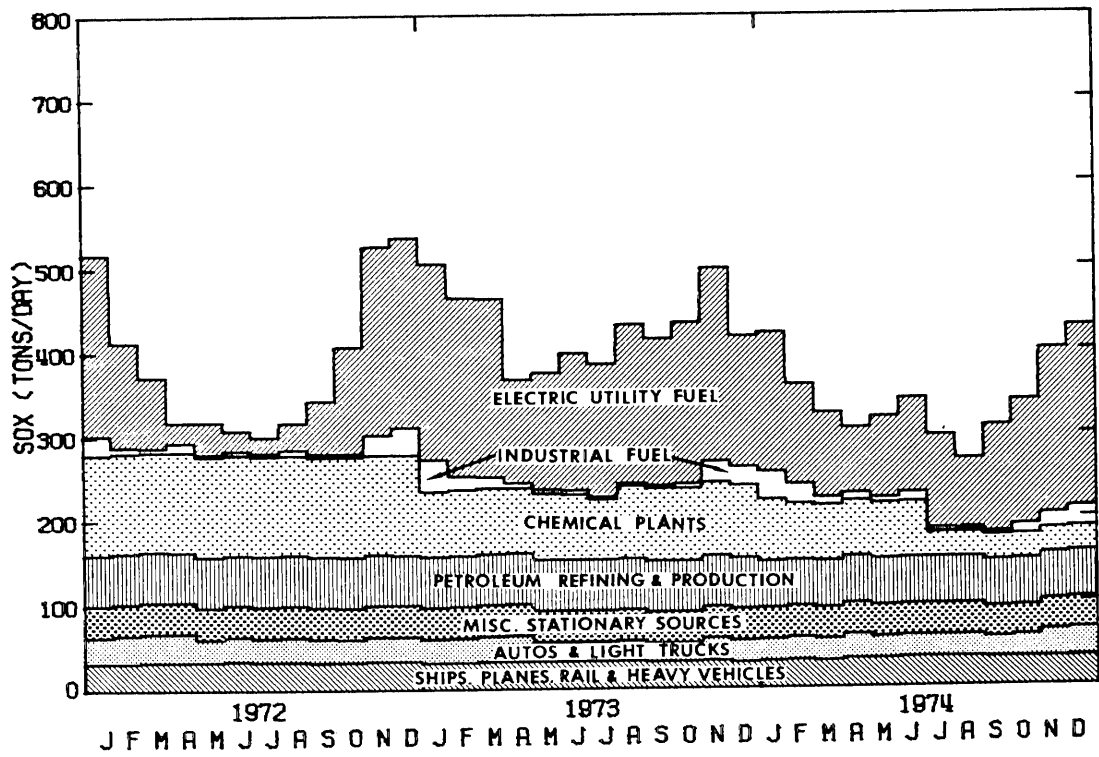


Figure 13

A strong seasonal variation in emissions from fuel burning sources is observed. Peak sulfur oxides emissions from electric utilities occur in the winter months as high priority home heating customers increase their consumption of natural gas forcing low priority gas customers, including electric utilities and some industries, to shift to combustion of sulfur-bearing fuel oil. An unusually severe test for our air quality model has been identified. A successful air quality model applied during these three years will have to be able to track strong seasonal changes in emissions source strength which are usually six months out of phase with the summer peak sulfate concentrations observed.

5.0 Results of the Air Quality Model Validation

The air quality dispersion model was applied to simulation of Los Angeles sulfate air quality over each month of the years 1972 through 1974. Model results closely reproduced observed sulfate concentration patterns within the central portion of the Los Angeles Basin, particularly during the years 1972 and 1973. Figures 14 through 18 outline air quality model results in time series at several widely separated air monitoring sites. In the upper graph of each pair, the sulfate air quality model results are represented by a continuous horizontal line which rises and falls over time. The small circles indicate the monthly means of sulfate observations at each monitoring site. The error bars represent a 95 percent confidence interval on the ambient air quality observations.

MONTHLY ARITHMETIC MEAN SULFATE CONCENTRATIONS AT DOWNTOWN LOS ANGELES (APCD)
AIR QUALITY MODEL RESULTS VS. OBSERVED VALUES

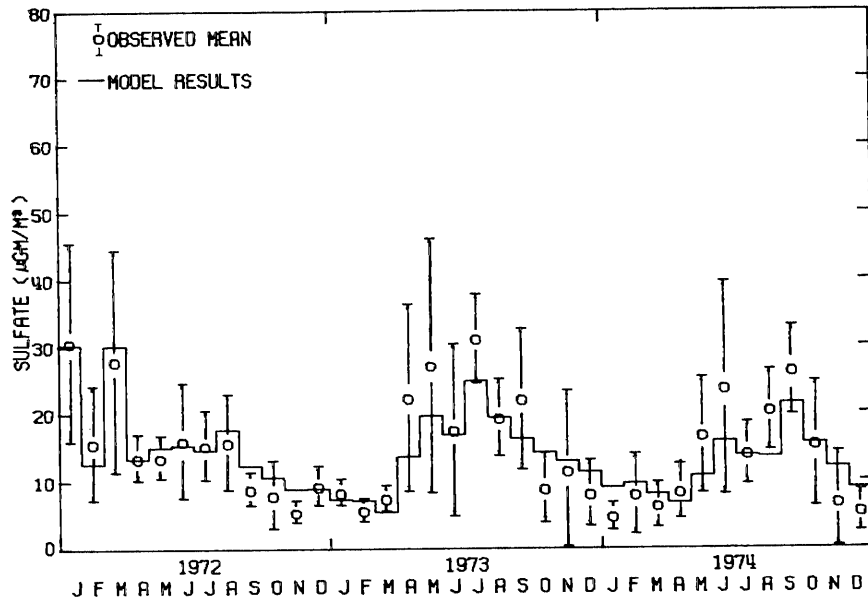


Figure 14a

SOURCE CLASS CONTRIBUTION TO SULFATE CONCENTRATIONS
OBSERVED AT DOWNTOWN LOS ANGELES (APCD)

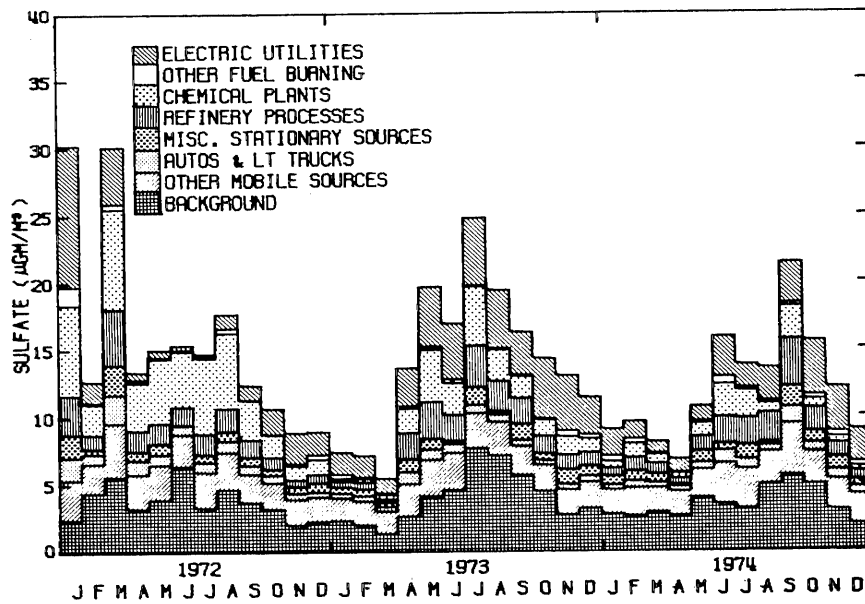


Figure 14b

MONTHLY ARITHMETIC MEAN SULFATE CONCENTRATIONS AT PASADENA (APCD)

AIR QUALITY MODEL RESULTS VS. OBSERVED VALUES

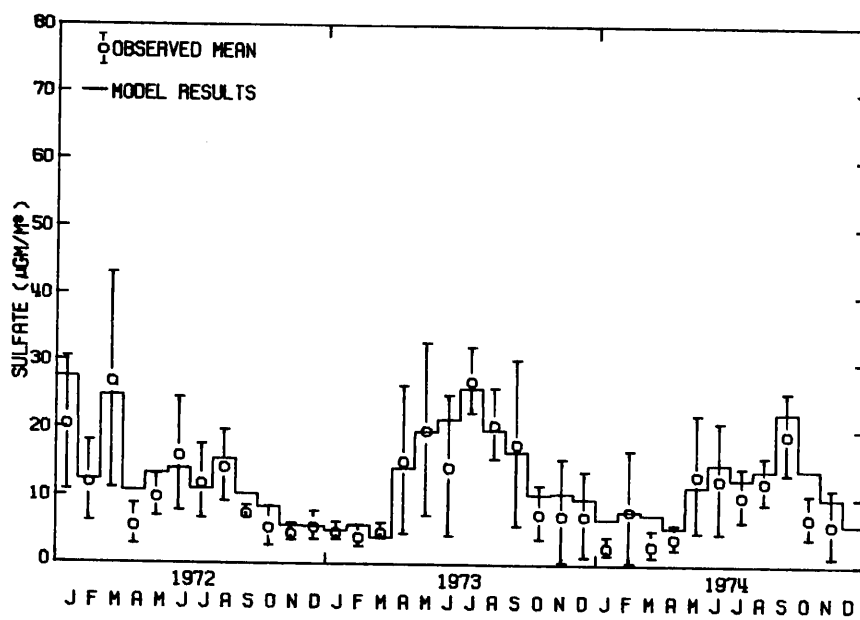


Figure 15a

SOURCE CLASS CONTRIBUTION TO SULFATE CONCENTRATIONS

OBSERVED AT PASADENA (APCD)

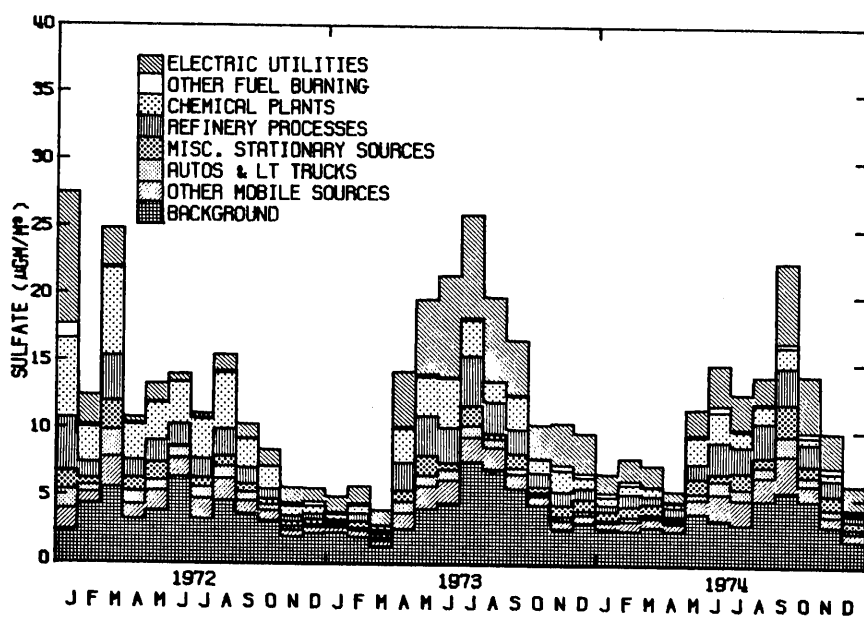


Figure 15b

MONTHLY ARITHMETIC MEAN SULFATE CONCENTRATIONS AT LENNOX (APCD)
AIR QUALITY MODEL RESULTS VS. OBSERVED VALUES

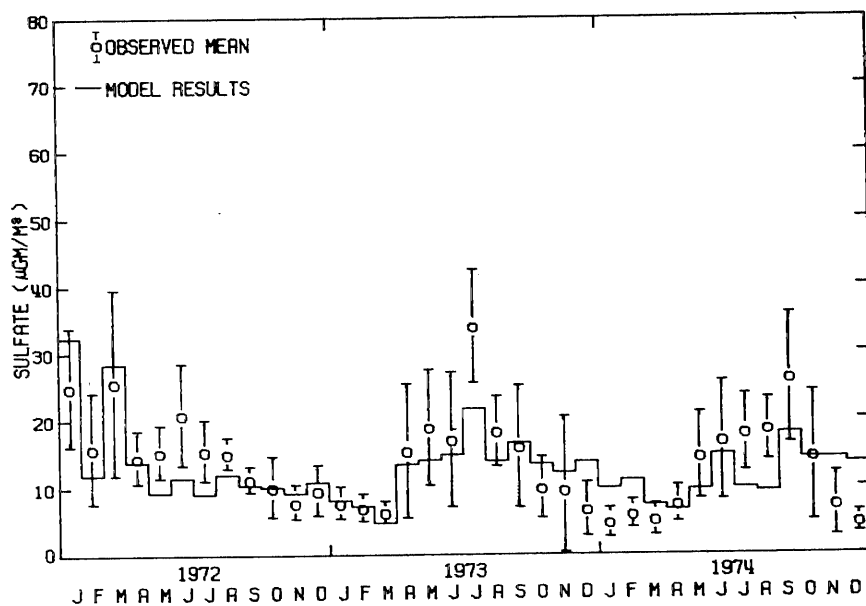


Figure 16a

SOURCE CLASS CONTRIBUTION TO SULFATE CONCENTRATIONS
OBSERVED AT LENNOX (APCD)

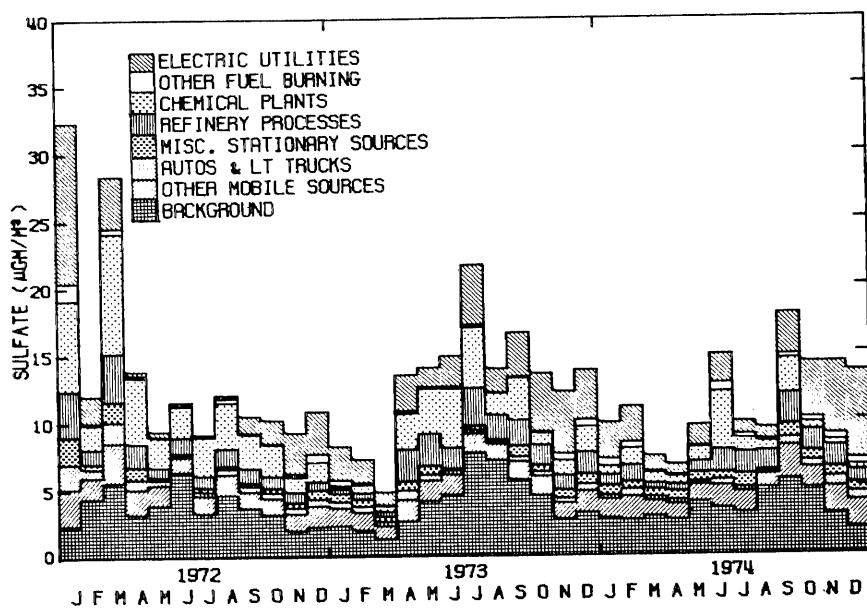


Figure 16b

MONTHLY ARITHMETIC MEAN SULFATE CONCENTRATIONS AT GLENDORA (CHESS)
AIR QUALITY MODEL RESULTS VS. OBSERVED VALUES

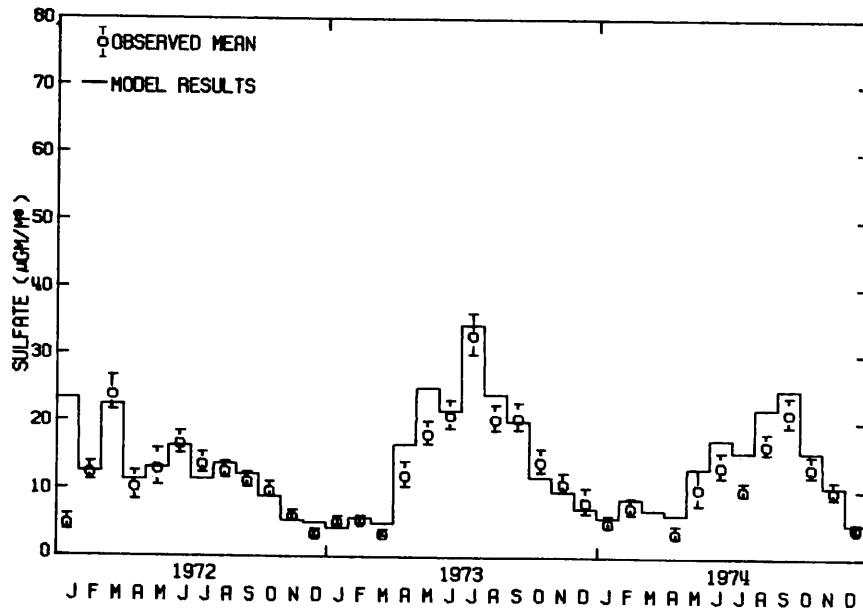


Figure 17a

SOURCE CLASS CONTRIBUTION TO SULFATE CONCENTRATIONS
OBSERVED AT GLENDORA (CHESS)

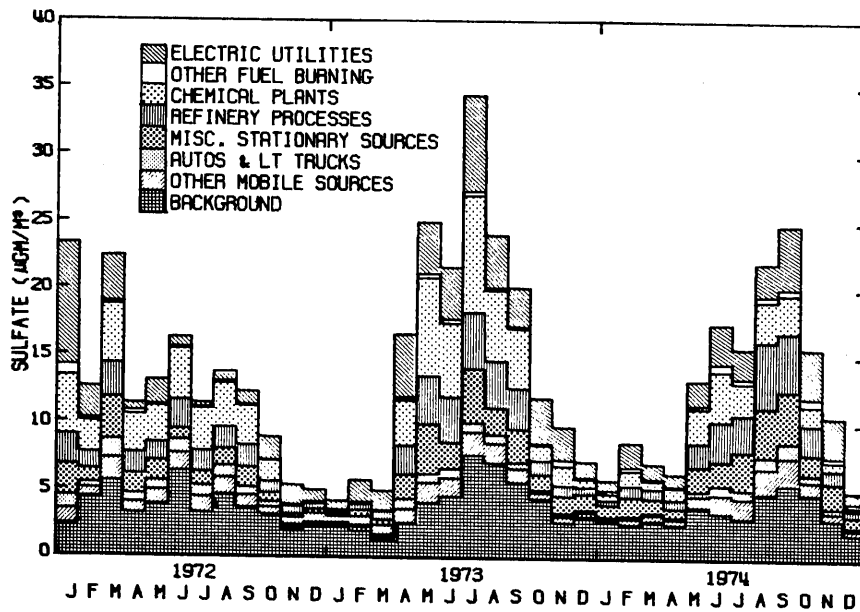


Figure 17b

MONTHLY ARITHMETIC MEAN SULFATE CONCENTRATIONS AT WEST LOS ANGELES (APCD)

AIR QUALITY MODEL RESULTS VS. OBSERVED VALUES

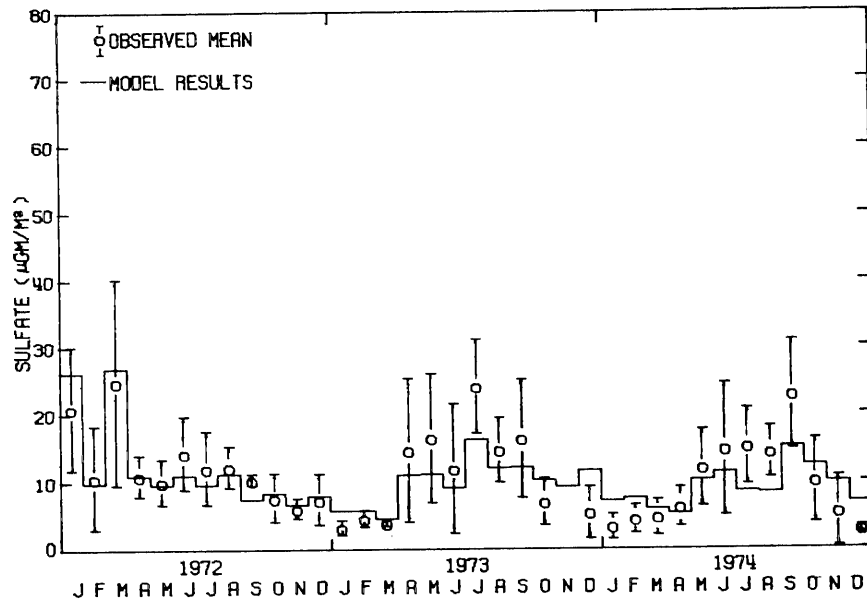


Figure 18a

SOURCE CLASS CONTRIBUTION TO SULFATE CONCENTRATIONS

OBSERVED AT WEST LOS ANGELES (APCD)

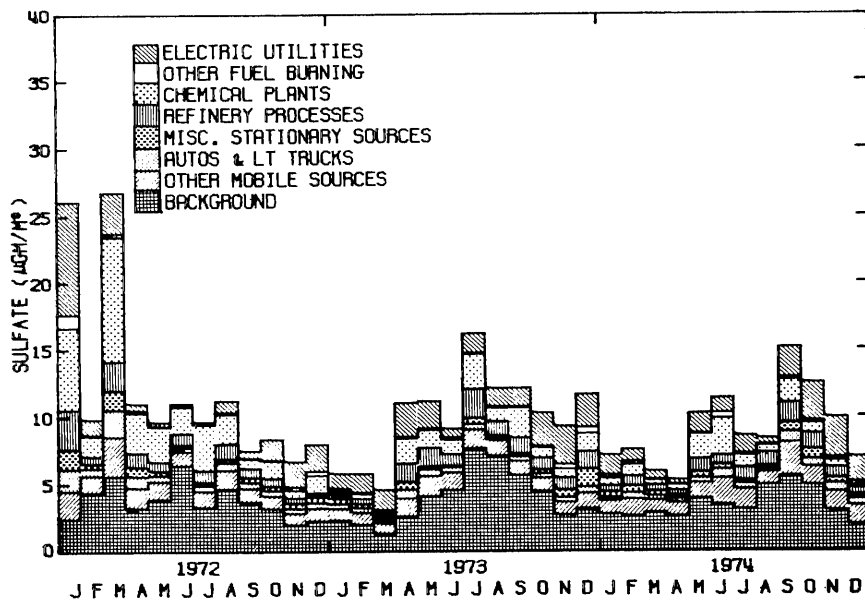


Figure 18b

Approximately 80 percent of the sulfate concentration predictions at LAAPCD air monitoring stations are within the error bounds on the ambient monitoring results. Model predictions track observed sulfate levels closely at the critical CHESS stations in the eastern San Gabriel Valley at Glendora and West Covina. A tendency to under-predict the summer peaks observed near the up-coast and down-coast edges of our study area at Santa Monica and at Garden Grove and Anaheim during 1973 and 1974 was noted. An illustration of the correlation between observed and predicted sulfate concentrations over all monitoring sites combined is given in Figure 19.

Source class increments to predicted sulfate air quality were examined in time series at each air monitoring station, as shown in the lower graphs of Figures 14 through 18. It was found that three to five source classes of roughly equal impact, plus background sulfates, must be considered simultaneously in order to come close to explaining sulfate levels observed at most locations. For example, during the year 1973 at downtown Los Angeles, contributors to the annual mean sulfate concentrations observed were estimated to be:

- Background sulfates - 28%
- Electric utility generating stations - 23%
- Heavy duty mobile sources - 15%
- Sulfur recovery and sulfuric acid plants - 12%
- Petroleum refining and production - 11%

SULFATE AIR QUALITY MODEL RESULTS - 1973
MONTHLY MEANS AT TEN AIR MONITORING STATIONS

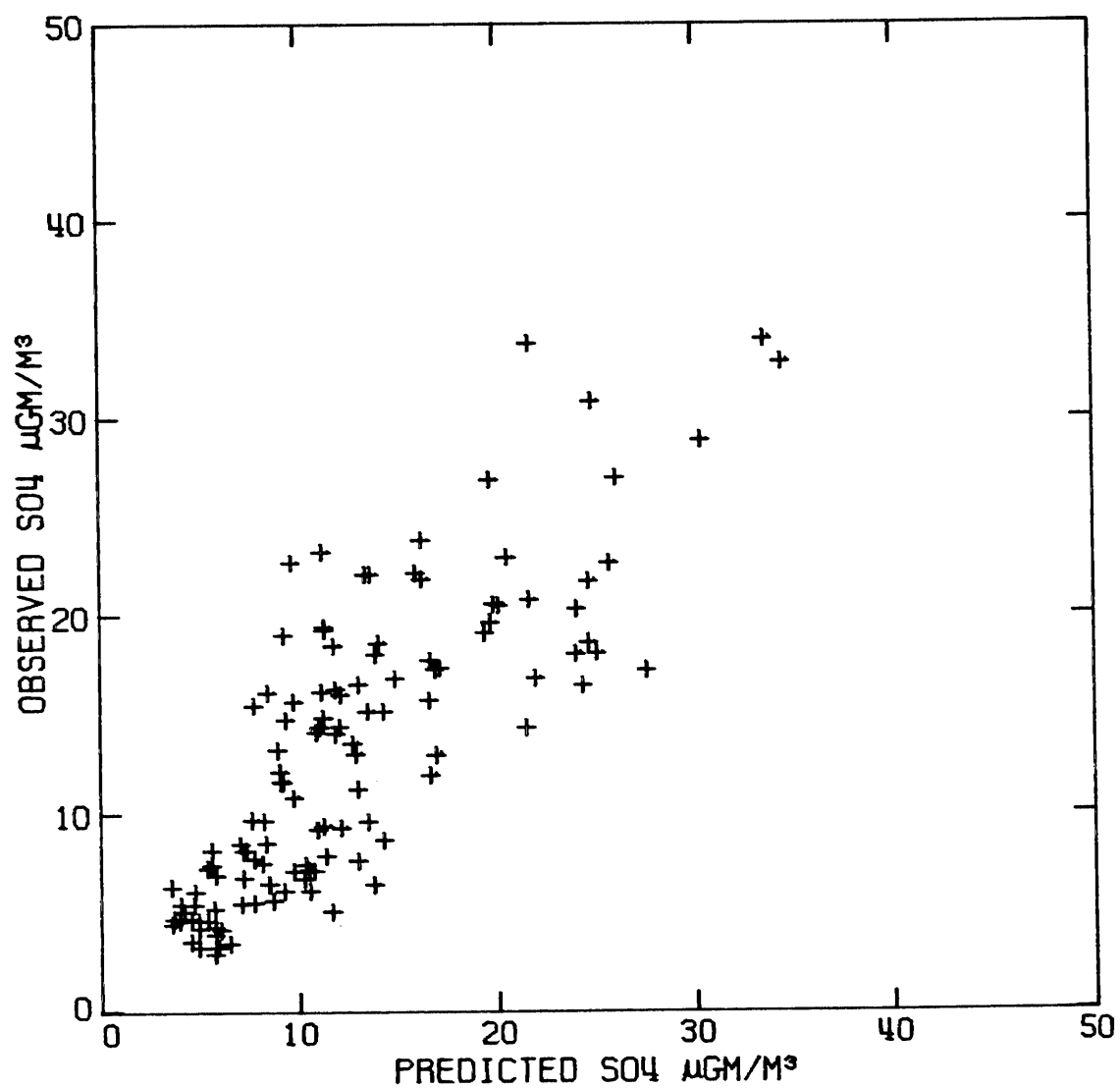


Figure 19

- Autos and light trucks - 4%
- Petroleum coke calcining kilns - 3%
- All remaining sources - 4%

The relative importance of particular source classes varies from one monitoring site to another, but no single source class clearly dominates the observed sulfate concentrations. The implication is that a mixed strategy targeted at a combination of source types will be needed if significant sulfate air quality improvements are to be achieved in this airshed through precursor SO_x control.

A seasonal variation in the overall rate of SO_2 oxidation in the Los Angeles atmosphere was inferred from simultaneous comparison of observations and model predictions at a large number of monitoring sites. As shown in Table 6, monthly mean SO_2 oxidation rates of between 0.5 percent per hour and 3 percent per hour prevail from October through February of our test years. During late spring, summer, and early fall, SO_2 oxidation rates were estimated to jump to an average of about 6 percent per hour, with individual months ranging ± 2 percent per hour about that mean value. Those numerical results must be qualified since a better understanding of seasonal trends in background sulfate concentrations or SO_2 deposition velocity could alter the outcome somewhat.

One striking feature of Los Angeles sulfate air quality is that average upwind/downwind concentration gradients observed between

TABLE 6

Calculated Rate of SO₂ Oxidation to Form Sulfates
in the Los Angeles Atmosphere, in Percent per Hour
(Overall Average Values of k for the Month Shown)

Month	1972	1973	1974	Three year mean
January	3%	1%	0.5%	1.5%
February	1%	1.5%	1%	1.2%
March	8%	1%	1%	3.3%
April	3%	5%	1%	3.0%
May	6%	8%	5%	6.3%
June	6%	7%	6%	6.3%
July	4%	8% ^(a)	5%	5.7%
August	5%	5%	8%	6.0%
September	4%	5%	8%	5.7%
October	2%	1%	3%	2.0%
November	1%	0.75%	1%	0.9%
December	1%	1%	0.5%	0.8%

Notes: (a) Average value from field measurement program in that month.
(Roberts, 1975)

monitoring sites are rather small in spite of the highly localized nature of major SO_x emission sources. Annual average sulfate air quality model predictions shown in Figures 20 through 22 confirm that observation: most monitoring sites lie within the 10 and 15 $\mu\text{gm}/\text{m}^3$ isopleths in all years of interest. The air quality model results of Figures 23 and 24 showing individual source class contributions to observed sulfate air quality help to explain this phenomenon. In winter months with a pronounced daily sea breeze/land breeze wind reversal, air parcel trajectories wander widely over the basin. Sulfur oxides emitted from all source classes are dispersed widely within the airshed by the rotation of the wind vectors. In contrast, during mid-summer, onshore flow persists for most of the day. However, the sequential siting of major SO_x sources along the coast means that the central portion of the air basin is downwind of one major source group or another at most times. Lateral dispersion of emissions is just about sufficient to balance sulfate formation, with the result that upwind/downwind pollutant gradients are rather small in spite of the direct inland transport from sources to receptors. Annual mean sulfate concentrations are further smoothed by seasonal transport cycles in which peak sulfate concentrations appeared far inland during the summer and near the coast during the winter.

In January 1972, extreme resultant wind stagnation occurred during a period of high SO_x emissions. The highest localized sulfate concentration predictions for any month of our three year period occurred at that time. While such extended stagnation is unusual, the

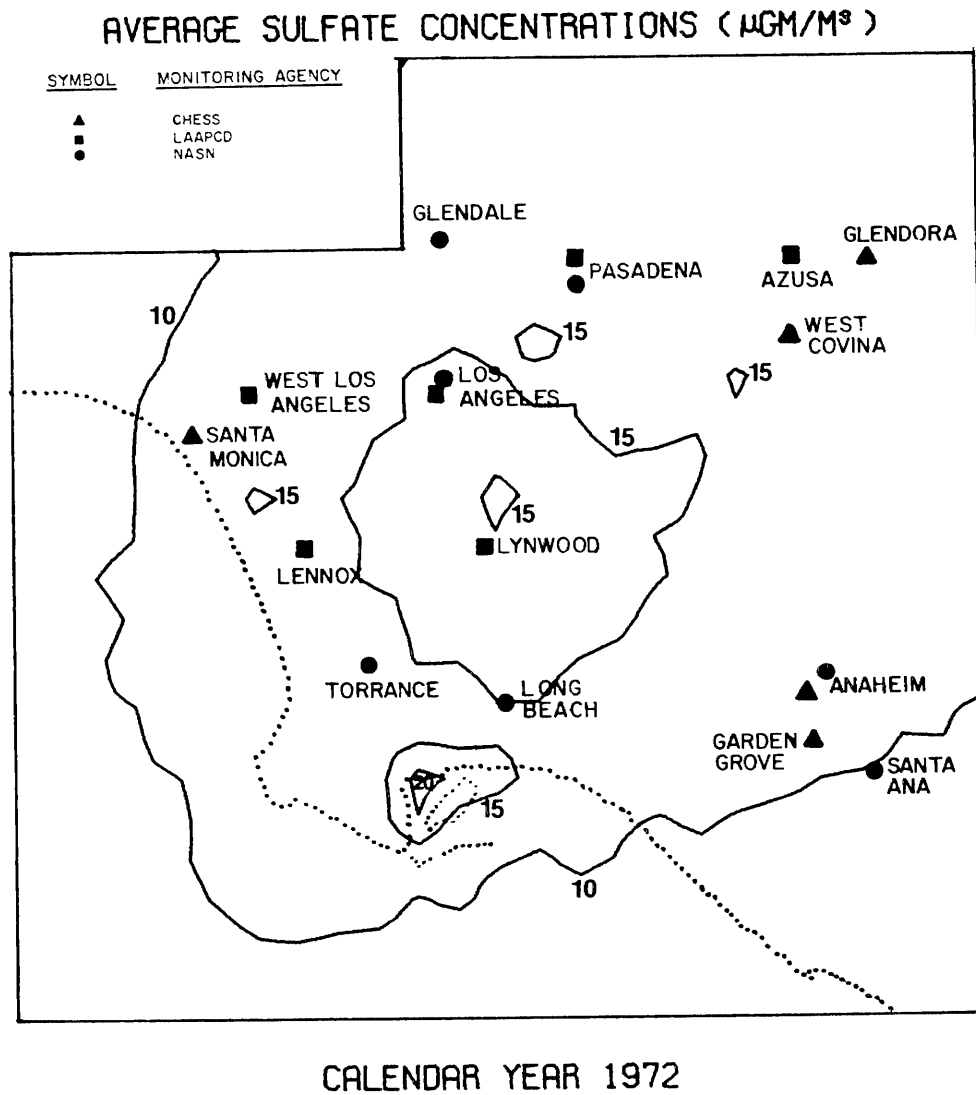
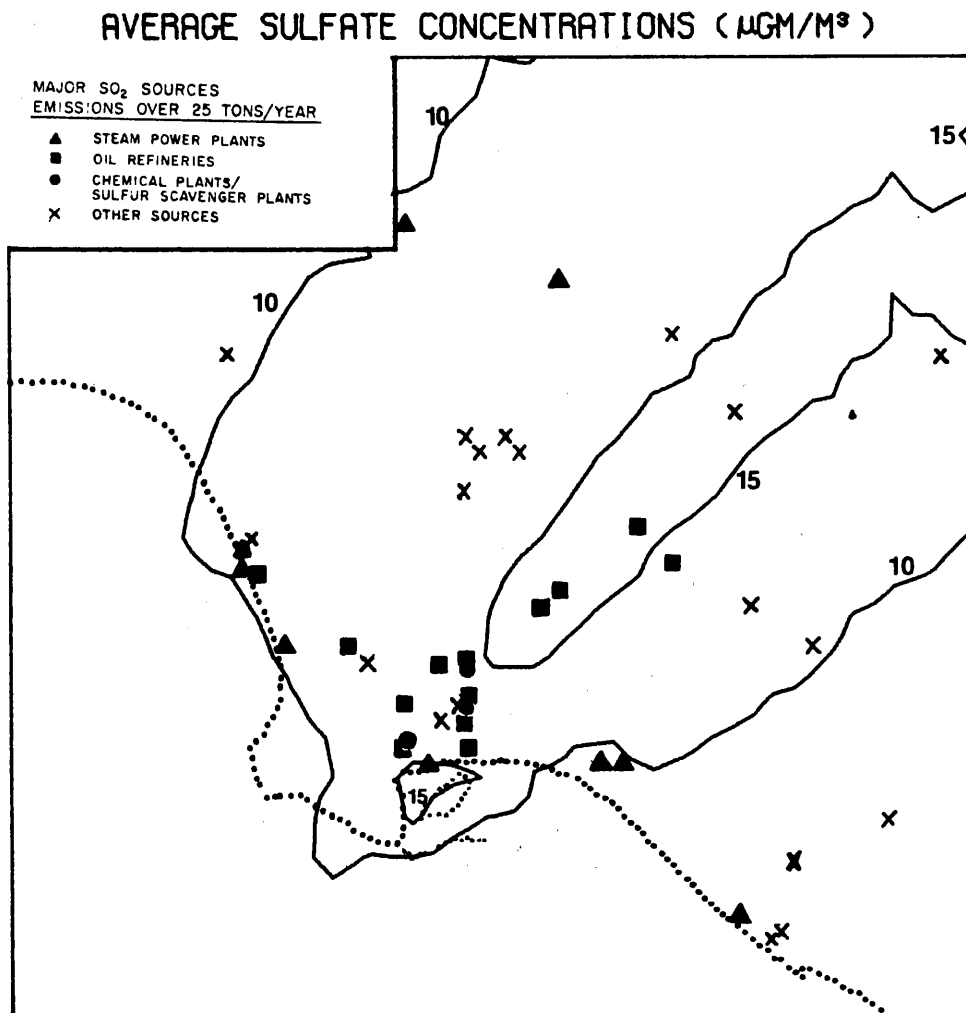


Figure 20



CALENDAR YEAR 1973

Figure 21

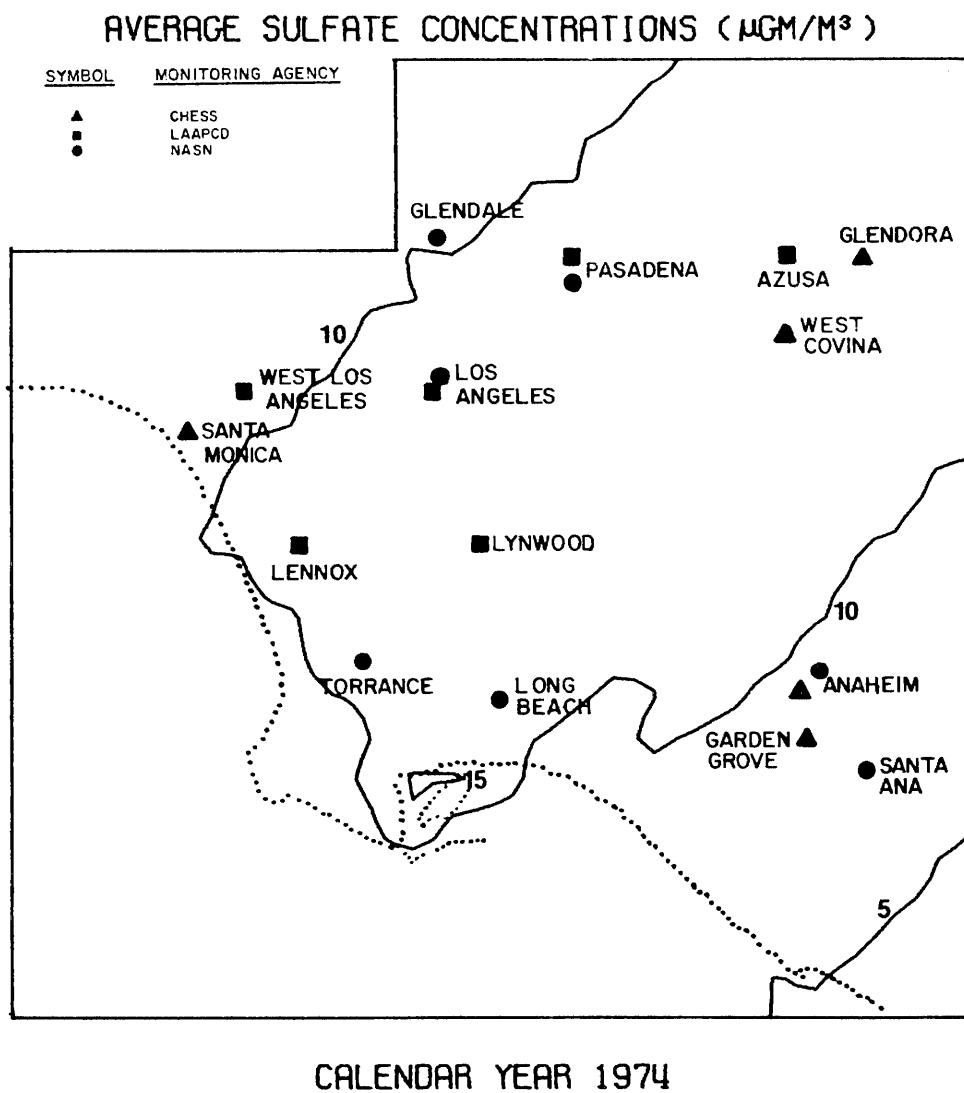
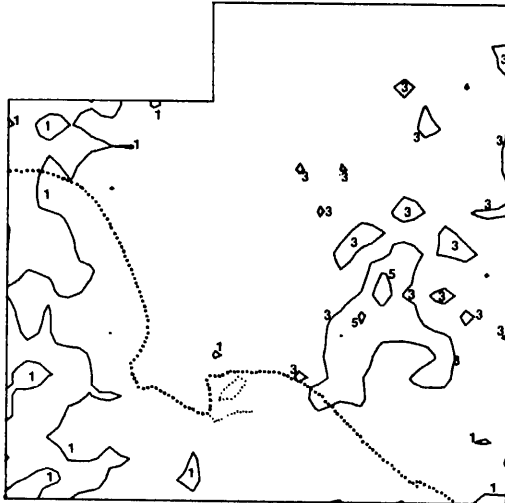


Figure 22

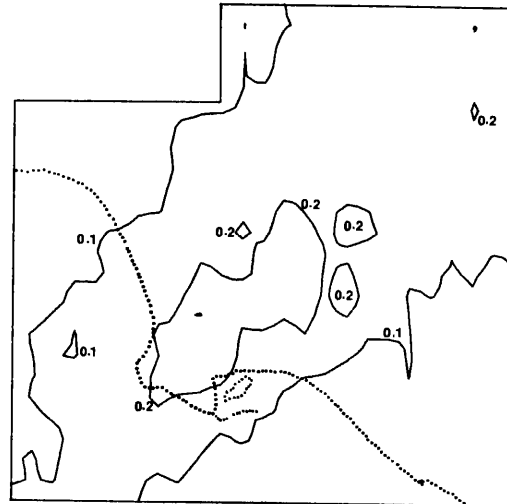
SULFATE AIR QUALITY INCREMENT DUE TO
ELECTRIC UTILITY BOILERS ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23a

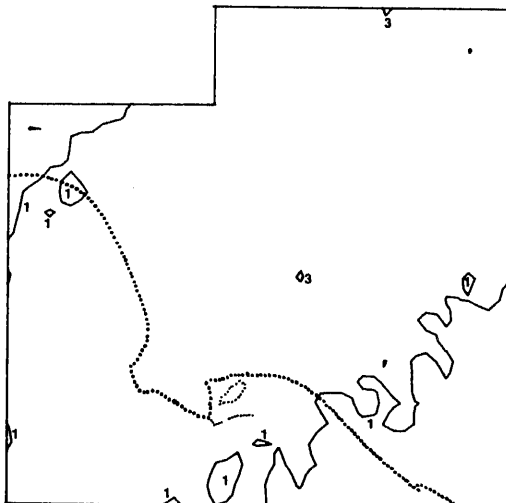
SULFATE AIR QUALITY INCREMENT DUE TO
OTHER FUEL BURNING SOURCES ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23b

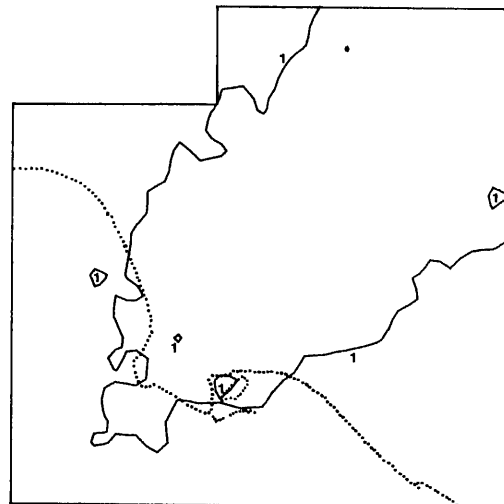
SULFATE AIR QUALITY INCREMENT DUE TO
CHEMICAL PLANTS ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23c

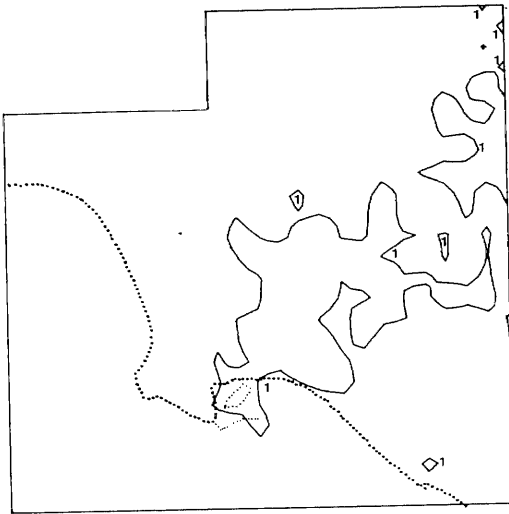
SULFATE AIR QUALITY INCREMENT DUE TO
PETROLEUM INDUSTRY PROCESSES ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23d

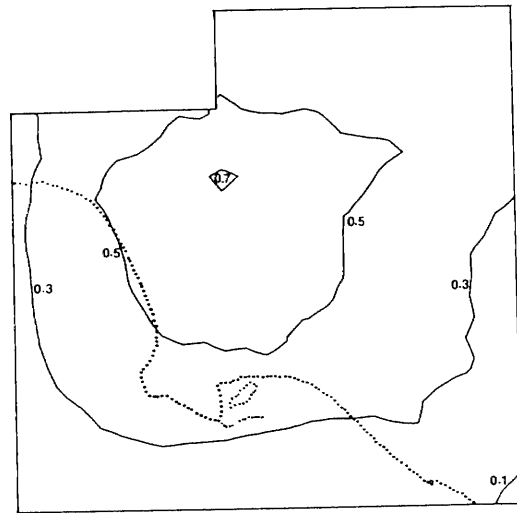
SULFATE AIR QUALITY INCREMENT DUE TO
MISCELLANEOUS STATIONARY SOURCES ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23e

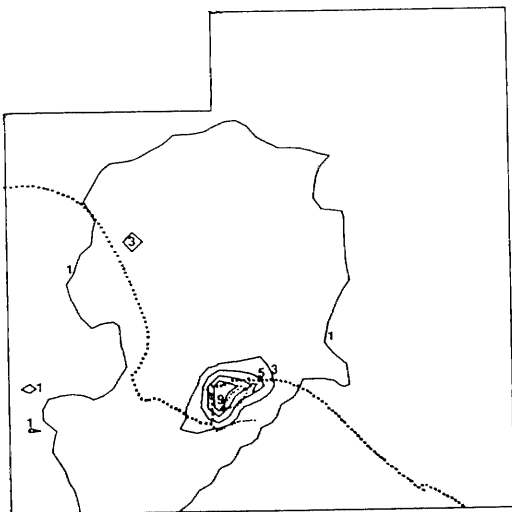
SULFATE AIR QUALITY INCREMENT DUE TO
AUTOS AND LIGHT TRUCKS ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23f

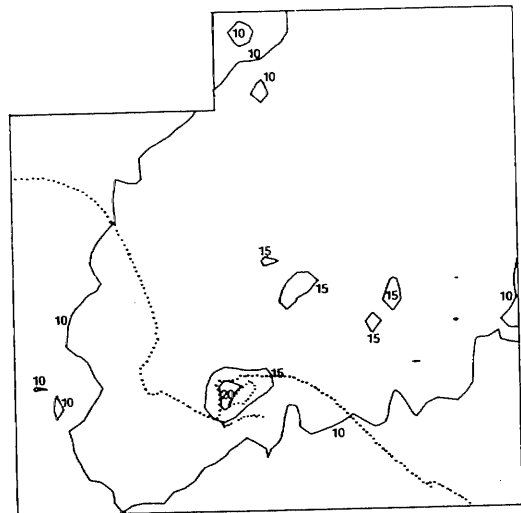
SULFATE AIR QUALITY INCREMENT DUE TO
OTHER MOBILE SOURCES ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23g

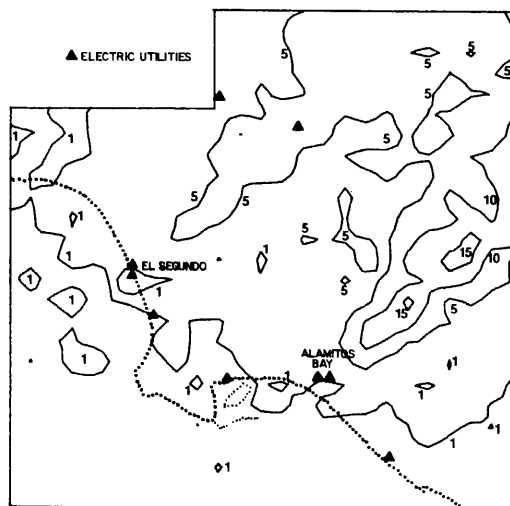
SULFATE AIR QUALITY INCREMENT DUE TO
ALL SOURCES PLUS BACKGROUND ($\mu\text{GM}/\text{M}^3$)



FEBRUARY 1972

Figure 23h

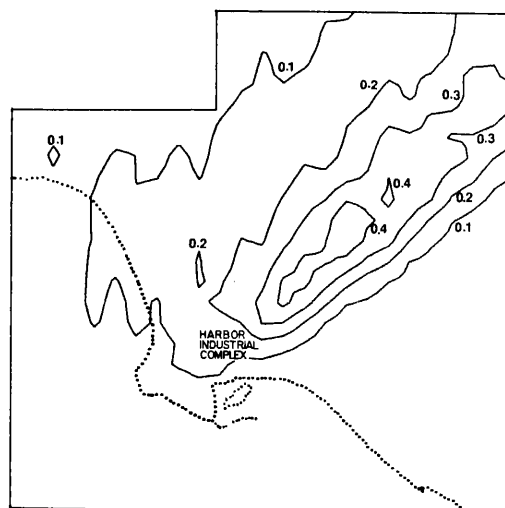
SULFATE AIR QUALITY INCREMENT DUE TO
ELECTRIC UTILITY BOILERS ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24a

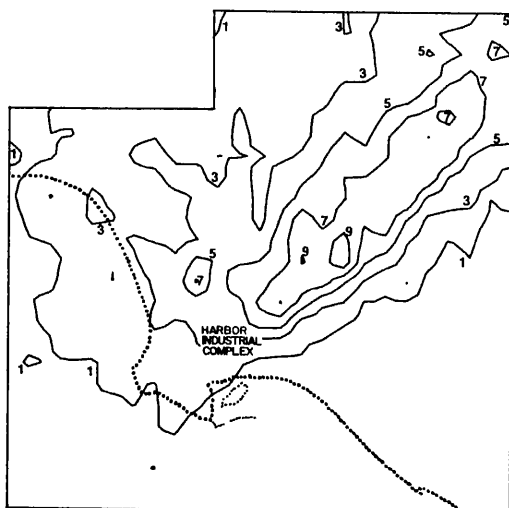
SULFATE AIR QUALITY INCREMENT DUE TO
OTHER FUEL BURNING SOURCES ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24b

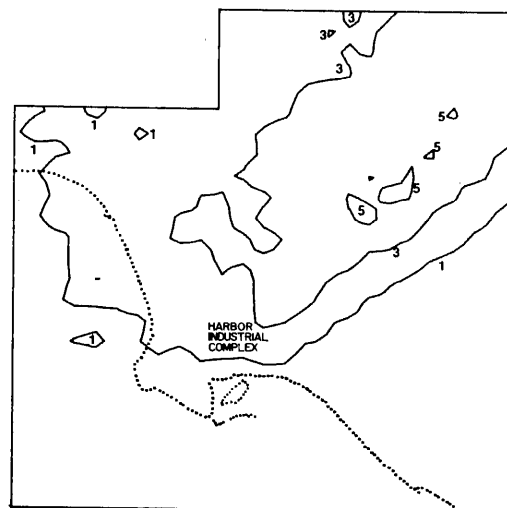
SULFATE AIR QUALITY INCREMENT DUE TO
CHEMICAL PLANTS ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24c

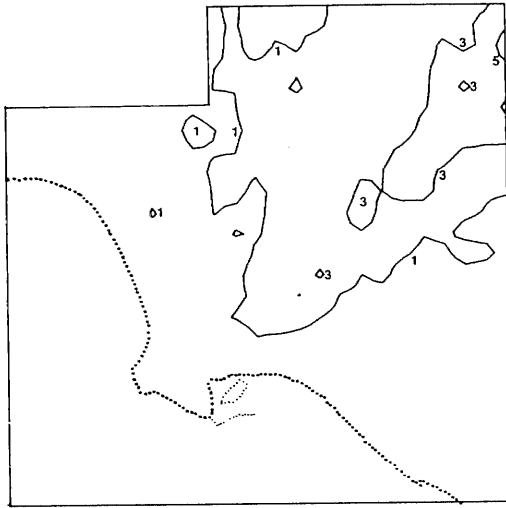
SULFATE AIR QUALITY INCREMENT DUE TO
PETROLEUM INDUSTRY PROCESSES ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24d

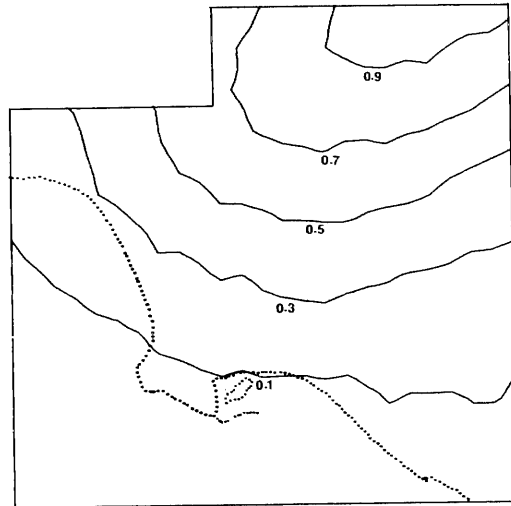
SULFATE AIR QUALITY INCREMENT DUE TO
MISCELLANEOUS STATIONARY SOURCES ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24e

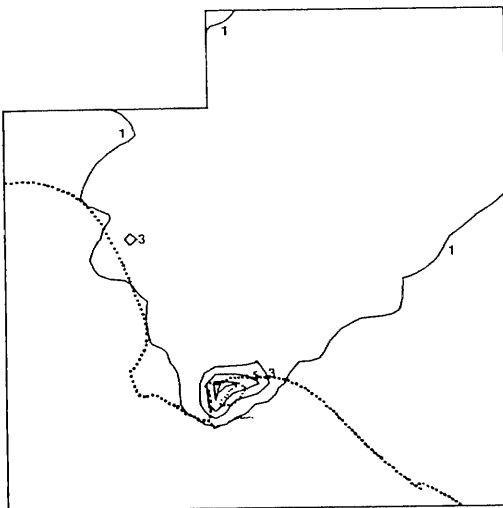
SULFATE AIR QUALITY INCREMENT DUE TO
AUTOS AND LIGHT TRUCKS ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24f

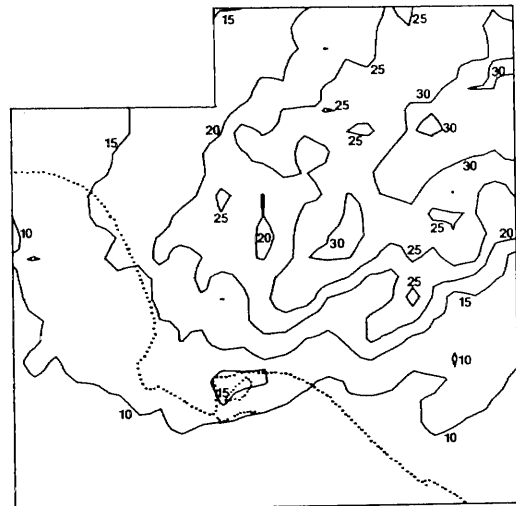
SULFATE AIR QUALITY INCREMENT DUE TO
OTHER MOBILE SOURCES ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24g

SULFATE AIR QUALITY INCREMENT DUE TO
ALL SOURCES PLUS BACKGROUND ($\mu\text{GM}/\text{M}^3$)



JULY 1973

Figure 24h

fact that it can occur means that sulfate air quality control strategy design must consider avoidance of wintertime as well as summertime pollution episodes in Los Angeles.

6.0 The Relationship Between Sulfate Air Quality and Visibility

Techniques were developed for analysis of the long-run impact of pollutant concentrations on visibility at downtown Los Angeles. Existing statistical models which use particle chemical composition as a key to particle size and solubility were reviewed. An analysis of vapor pressure lowering over solutions of electrolytes was used to add structure to these models so that the relative humidity dependence of light scattering by hygroscopic aerosols could be represented in a more physically realistic manner. Light absorption by NO_2 was added to the analysis.

Coefficients were fit to the model based on air pollution control agency routine air monitoring data taken at downtown Los Angeles over the decade 1965 through 1974. It was found that principal contributors to visibility reduction at downtown Los Angeles include sulfates and oxides of nitrogen (NO_2 and nitrates). There is a pronounced increase in light scattering per unit sulfate solute mass on days of high relative humidity, as would be expected for a hydroscopic or deliquescent substance. Light extinction by SULFATES was quantified as $0.107 (1-\text{RH})^{-0.53} (10^4 \text{m})^{-1}$ per $\mu\text{gm}/\text{m}^3$, where RH stands for relative humidity in (%/100) and SULFATES is taken as 1.3 times the measured $\text{SO}_4^{=}$ concentration in order to account for the mass of associated cations.

That functional relationship between light extinction by sulfates and relative humidity was compared to theoretical calculations for light scattering by ammonium sulfate aerosols. Our results were found to be similar in shape but slightly higher than the theoretical calculation would indicate. These small differences between theory and analysis of Los Angeles observations may be due to the deviation of an actual human observer's visual acuteness from that assumed by Koschmieder.

Having developed and fitted a model representing a decade of atmospheric events, it becomes possible to examine the likely long-run response of visibility in the Los Angeles basin to altered levels of particulate sulfates. It was estimated that the visibility impact of reducing sulfates to a half or to a quarter of their measured historic values on each past day of record would be manifested most clearly in a reduction of the number of days per year with average visibility less than three miles. For example, as shown in Figure 25, a 50 percent reduction in sulfates levels on a daily basis would have reduced the number of days with worse than three-mile visibility by about one half, while improvement in the number of days of average visibility greater than ten miles would be much smaller, about 10 percent.

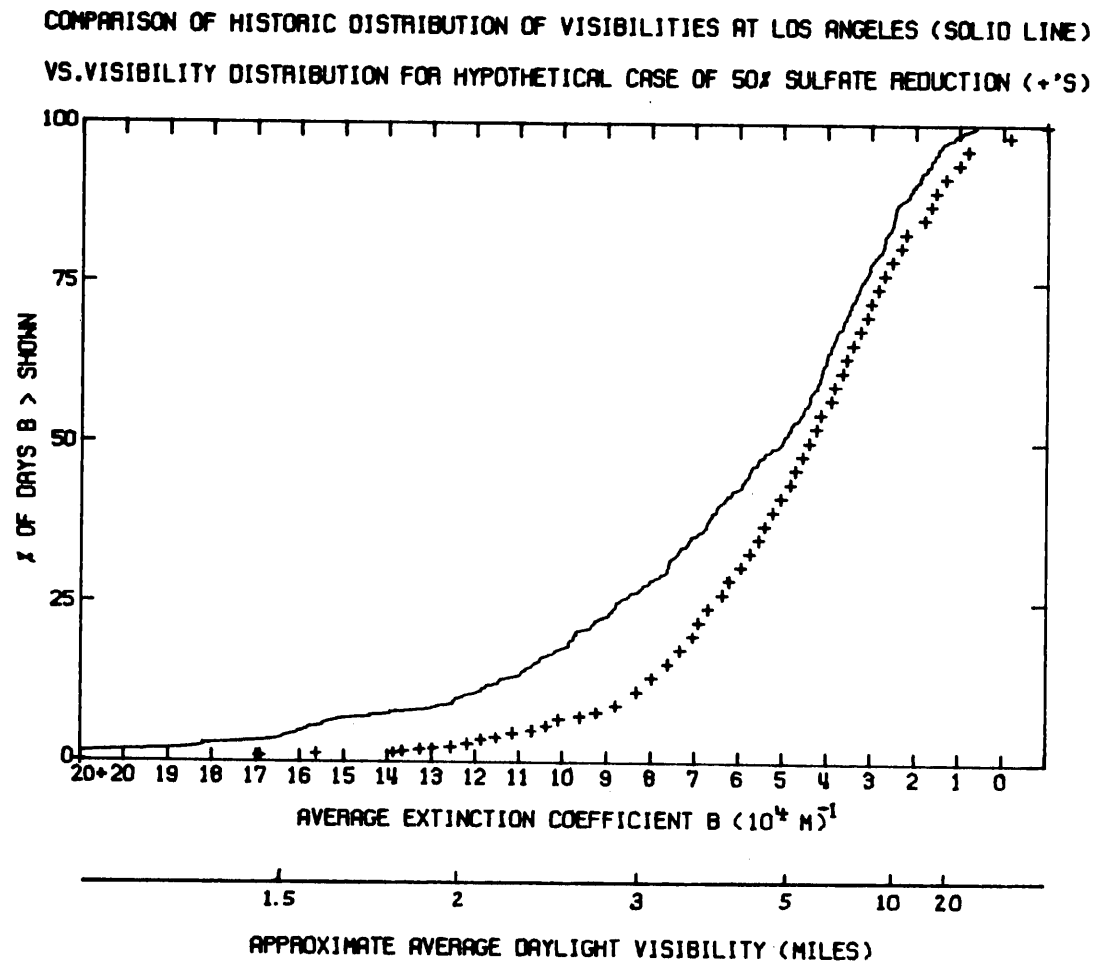


Figure 25

7.0 Toward Emission Control Strategy Analysis

The results of the air quality and visibility models can be used to evaluate sulfate air quality control strategy options. Example calculations worked for the year 1973 in Figure 26 show that a 43 percent reduction in annual mean sulfate concentrations at downtown Los Angeles could have been achieved in that year through application of the SO_x emission control technologies suggested by Hunter and Helgeson (1976). A second strategy predicted in part on deregulation of the price and availability of new natural gas supplies to industry could have achieved about a 49 percent decrease in sulfate concentrations in 1973 at lower cost than a purely technological solution to the Los Angeles sulfate problem.

STATIONARY SOURCE EMISSION CONTROLS
IDENTIFIED BY HUNTER AND HELGESON (1976)
APPLIED TO SO_x EMISSIONS SOURCES LOCATED
IN THE SOUTH COAST AIR BASIN
AS THEY EXISTED IN 1973

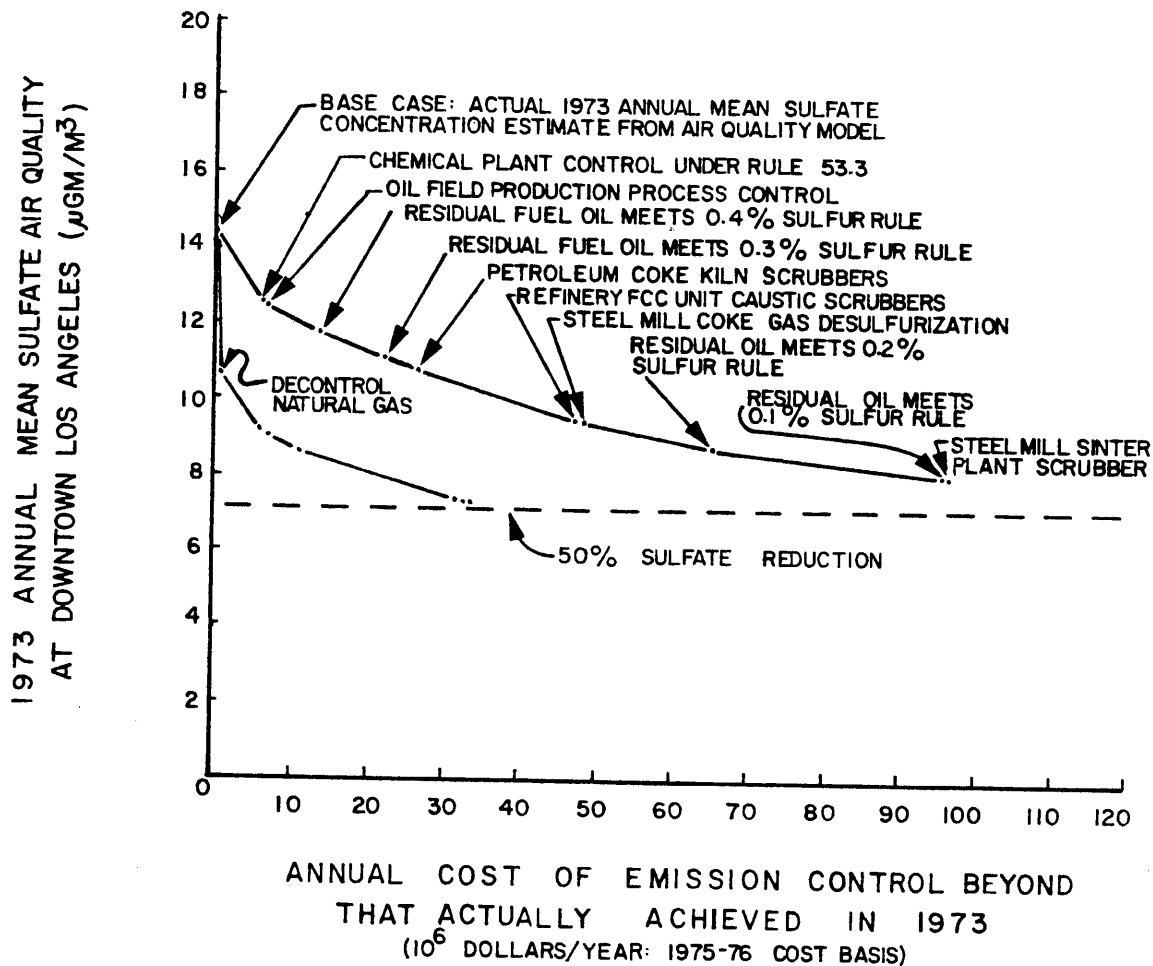


Figure 26

NOTE: This figure accompanies a sulfate air quality control strategy example calculation. It applies to conditions in that airshed as they existed in 1973. Further reductions in natural gas supply beyond the levels of service observed in 1973 will greatly increase the annual cost of the emissions control strategy pictured in the upper curve of this graph. Changes in assumptions about emissions control technology or clean fuel availability and price could significantly alter the cost effectiveness shown. This figure was constructed to illustrate the means by which the description of airshed physical processes developed in this study can be used almost immediately to formulate emission control strategies for sulfates in the South Coast Air Basin. It should not be interpreted as containing a control strategy recommendation. (Reproduction of this figure without this caption will not be authorized.)

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